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16. ABSTRACT

The report covers EPA's third symposium on the environmental aspects of fuel conversion technology. The symposium was conducted in Hollywood, Florida, September 13-16, 1977. Its main objective was to review and discuss environmentally related information in the field of fuel conversion technology. Specific topics were program approach, environmental assessment, and control technology development.

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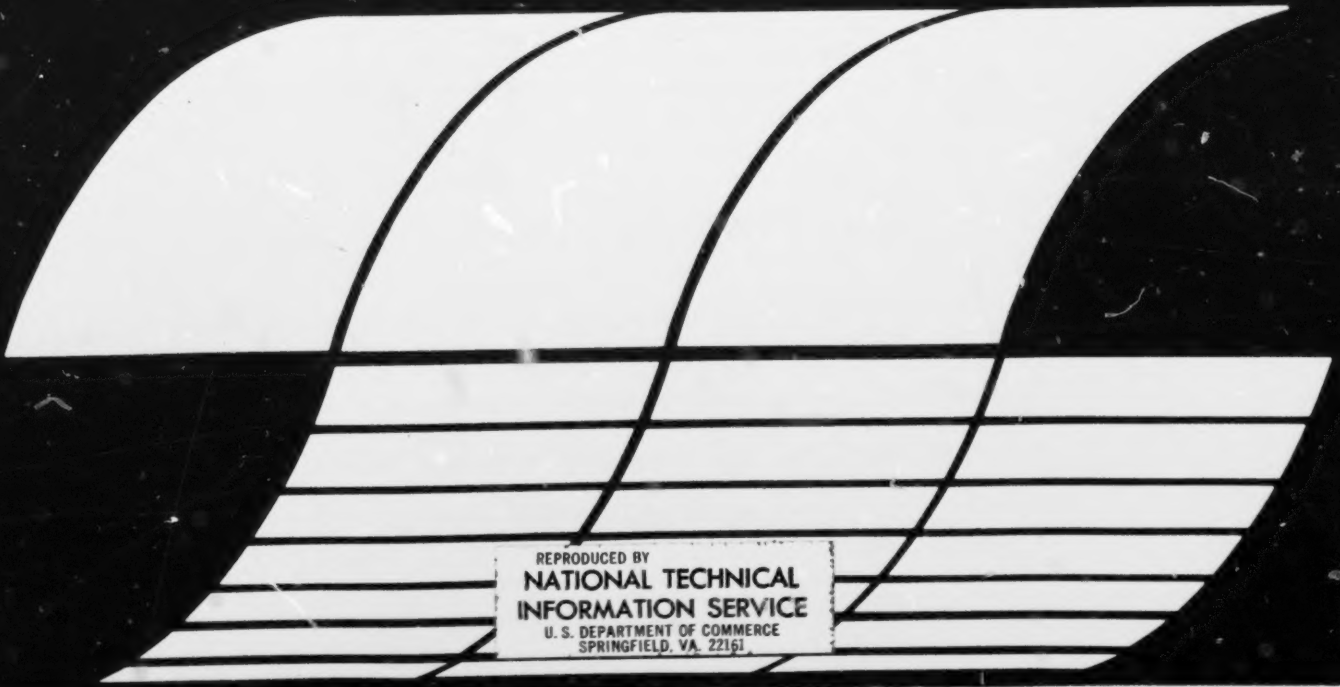

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SYMPOSIUM PROCEEDINGS:
Environmental Aspects of Fuel Conversion Technology, III
(September 1977, Hollywood, Florida)

Franklin A. Ayer and Martin F. Massoglia, Compilers

Research Triangle Institute
P. O. Box 12194
Research Triangle Park, N. C. 27709

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Industrial Environmental Research Laboratory
Office of Energy, Minerals and Industry
Research Triangle Park, N.C. 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

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FOREWORD

The proceedings for the symposium on "Environmental Aspects of Fuel Conversion Technology, III" is the final report submitted to the Industrial Environmental Research Laboratory for the Environmental Protection Agency Contract No. 68-02-2612. The symposium was held at the Diplomat Hotel, Hollywood, Florida, September 13-16, 1977.

The main objective of the symposium was to review and discuss environmentally related information on coal conversion technology. Papers were presented that covered a summarization of major environmental programs and contaminants in coal, process technology, control technology, process measurements, sampling and analytical information pertinent to coal gasification and liquefaction, and product usage.

Mr. William J. Rhodes, Chemical Engineer, Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, was the Project Officer and General Chairman of the Symposium.

Mr. Franklin A. Ayer, Manager, Technology and Resource Management Department, Center for Technology Applications, Research Triangle Institute, Research Triangle Park, North Carolina, was the Symposium Coordinator and Mr. Ayer and Dr. Martin F. Massoglia of the same Department were Compilers of the proceedings.

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KEYNOTE ADDRESS

Frank T. Princiotta
Office of Energy, Minerals, and Industry
U.S. Environmental Protection Agency
Washington, D.C.

It is a pleasure to participate in the Third Symposium on the Environmental Aspects of Fuel Conversion Technology. I would like to thank John Burchard and Robert Hangebrauck for their kind invitation, and I hope I can make some remarks relevant to the important work you are engaged in. Since many of you are concerned with environmental pollution from various fuel conversion technologies, I think it might be relevant if I would discuss the recently signed into law Clean Air Amendments of 1977.

These Amendments supercede the Clean Air Amendments of 1970. At the time the 1970 Amendments were enacted into law, this was considered the most significant piece of environmental legislation in the United States' history. The 1977 Amendments build upon the 1970 Amendments and in many ways supplement or strengthen the earlier legislation. At the outset, I should point out the complexity of this new law and the fact that EPA is only now attempting to interpret this legislation. In many ways our EPA Air Programs Office is the equivalent of a biblical scholar, attempting to understand and interpret the Clean Air Amendments as the scholar would the Bible.

Although I will attempt to summarize some of the more important aspects of this new law, with emphasis on those provisions that relate to energy sources, I strongly suggest you carefully read the Act for yourselves.

The Amendments are divided into four titles. Title I concerns itself primarily with stationary sources, Title II provides guidance on mobile pollution sources, and Titles III and IV are more in the miscellaneous category. I would like to discuss several of the important Sections in Title I relating to stationary sources. Specifically, I would like to summarize what the new Act says regarding new source standards of performance (Section 109), the standards for hazardous air pollutants (Section 110), unregulated pollutants (Section 120), prevention of significant deterioration (Section 127), and nonattainment areas (Section 129).

New Source Standards of Performance (Section 109)

This section amends the existing Section 111 and expands the concept of setting technologically based standards for the control of air pollution from new pollution sources.

The section requires that major new sources use the best technological continuous emission controls to meet new source standards of performance. Essentially this eliminates the use of intermittent or alternative control measures and the use of low sulfur fuel as an acceptable control approach. Specifically, this section states that the best adequately demonstrated technology, (including pre-combustion cleaning or treatment of fuels) is to be the basis of the standard. It requires the Administrator to take into account energy requirements in determining which technologies have been adequately demonstrated. Also, the Administrator must consider nonair quality, health, and environmental impacts in making the determination.

This section activates a timetable for the consideration of setting standards for additional sources of air pollution. Specifically, the Amendments allow one year for additional listing of sources and at least one-quarter of the standards must be promulgated at the end of the second year of listing, at least three-quarters by the end of the fourth year of listing. The Administrator is also asked to consider the adequacy of existing new source performance standards at least every four years. The implication of this is that as the control technology improves, standards should be tightened.

Guidance is provided for the setting of new source performance standards specifically for fossil fuel-fired boilers. The Act calls for present standards to be revised and to include a percentage emission reduction in pollution from untreated fuel as well as a standard of performance. In calculating the percentage reduction requirement, the Administrator is authorized to give credit for accepted mine mouth and other precombustion fuel cleaning processes, whether they occur at, or are achieved by, the source of by another party.

Waiver for Technology Innovation (Section 109)

The Amendments provide a mechanism for the Administrator to grant waivers of up to 7 years after the date on which the first waiver is granted or 4 years after commencement of operation, from Federal new source performance standards to permit a source to use innovative continuous emission control technology.

In order to grant such a variance, the Administrator must find:

1. A substantial likelihood that the new technology will achieve greater emission reduction than that required under the new source performance standard, or equivalent reduction at lower economic, energy, or environmental costs;
2. The new technology will not cause or contribute to an unreasonable risk to public health, welfare, or safety;
3. The governor of the state in which the source requesting variance is located consents to the waiver;
4. The waiver will not prevent the attainment or maintenance of any national ambient air quality standard;
5. The proposed system has not been adequately demonstrated; and
6. In determining the substantial likelihood of a new system achieving greater emission reduction, the Administrator must take into account any previous failures of the system.

Hazardous Design Standards (Section 110)

This provision amends the old Section 112 of the existing law to allow the specification of design, equipment, or operational standards for the control of the source of hazardous emissions, where an emission limitation is not possible or feasible.

Unregulated Pollutants (Section 120)

EPA has 1 year to determine whether cadmium, arsenic, and polycyclic organic matter (2 years for radioactive pollutants) cause or contribute to air pollution and endanger public health, before regulating them under this act. Also, within 1 year the Administrator must consider the promulgation of a short term NO_2 ambient air quality standard for a period not to exceed 3 hours.

Prevention of Significant Deterioration (Section 127)

The Clean Air Amendments of 1970 activated a schedule that aimed at improving air quality in polluted areas so that health and welfare were protected. However, the Act did not contain a provision for protecting airsheds that were not beyond those pollution levels considered detrimental to health and welfare. The Amendments of 1977 add an important provision for the prevention of significant air quality deterioration in areas where pollution levels are lower than existing standards. This provision defines three air quality categories. Class 1 allows only a small increment of additional pollution; Classes 2 and 3 allow corresponding greater amounts of pollution. The Act classifies the following as mandatory Class 1 Federal areas:

1. International parks;
2. Wilderness areas (in access of 5000 acres);
3. National memorial parks (in excess of 5000 acres); and
4. National parks (in excess of 6000 acres).

Initially all other areas are considered Class 2 areas. However, states can in certain circumstances redesignate such areas as Class 1 or as the less restrictive Class 3 category.

This section delineates allowable increments of pollution above baseline concentration for each of the three classes for sulfur dioxide and particulates. Within 2 years, states must submit plans establishing increments or other means of preventing significant deterioration from the other criteria pollutions, namely: nitrogen oxides, hydrocarbons, carbon monoxide, and oxidants. EPA must approve the plan within 4 months if it meets applicable requirements; otherwise EPA must propose a plan for the rejected state within 4 months of the disapproval. States may exempt certain emissions such as those from facilities converting from oil or gas to coal, natural gas curtailments, temporary construction, and foreign sources from being counted against the increment.

In order to protect Class 1 areas which could be affected, no major emitting facility can be constructed without a permit establishing emission limitations. Extensive studies will be required in order for permits to be issued for major emitting facilities that could affect Class 1 areas. For example, the EPA must: require an analysis of the ambient air quality, climate and meteorology, terrain, soils and vegetation, and visibility at the site of the proposed major emitting facility; and in the area potentially affected by the emissions from such a facility for each pollutant regulated under this act, determine the degree of the continuous emission reduction which could be achieved by such a facility.

Requirements for Nonattainment Areas (Section 129)

Another area that was not dealt with in the 1970 Amendments was the question of siting new plants in nonattainment areas, i.e., those areas that are polluted above those levels being necessary to protect health and welfare. What the new legislation does is essentially validate the offset policy published by EPA in December, 1976. In order to issue a permit to a major new source in a nonattainment area, the state must show that total emissions from all sources in the region will be sufficiently less than the total emissions allowed for existing sources prior to the construction of the major new source. Thus the baseline for calculating offsets is the total emissions allowed in the implementation plan without taking the new source into consideration. As a condition for permitting major new stationary sources to locate in nonattainment areas, the states are required to have approved revised implementation plants. The plans must provide for attainment of primary ambient standards (health-related standards) no later than December 31, 1982, although attainment can be delayed until December 31, 1987 with respect to photochemical oxidants and carbon monoxide. The State Implementation Plan (SIP) must, among other things, provide for utilizing "all reasonably available control measures as expeditiously as practicable." It must also specifically identify and quantify all emissions which will result from the construction and operation of a major new or modified stationary source. The SIP revision must include a permit program for stationary sources to allow a source-by-source or area-wide tradeoff policy; new sources must achieve "lowest achievable emission rate." reflecting the most stringent emission limitation that is contained in the SIP of any state for such class or category of source, or the most stringent emission limitation that is achieved in practice, whichever is more stringent.

In conclusion, I have attempted to give you a flavor for the content, importance, and the complexity of this new legislation. Even now the EPA lawyers and technical people are trying to interpret this intricate piece of legislation. Although it is too early to quantify the impact of the law, it is clear to me that the effect of this legislation will be far-reaching and will be a major factor in influencing the development and utilization of emerging energy technologies.

Session I: PROGRAM APPROACH

Forest O. Mixon
Chairman

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THE SYNTHETIC FUELS PROGRAM OF THE FUEL PROCESS BRANCH OF THE IERL-RTP

T. Kelly Janes
Fuel Process Branch,
Industrial Environmental Research
Laboratory-RTP,
U.S. Environmental Protection Agency
Research Triangle Park, N.C.

The Industrial Environmental Research Laboratory conducts a contractual and in-house research, development, and demonstration program dealing with the control of emissions/discharges from energy related technologies and industrial processes.

The Laboratory is divided into three technical divisions (figure 1):

1. Utilities and Industrial Power Division which primarily addresses the emissions controls for the combustion of fossil fuels to generate steam and electrical power.
2. Energy Assessment and Control Division which develops improved combustion techniques for nitrogen oxide control, advanced combustion systems, and the environmental effects and control techniques for coal processing and conversion of coal to synthetic liquids and gases.
3. Industrial Processes Division which addresses the emission and controls from industrial operations. Additionally, in this Division, analytical and sampling techniques are developed.

The Fuel Process Branch in the Energy Assessment and Control Division conducts programs addressing two major areas (figure 2):

1. *Coal Cleaning.* Development of physical and chemical techniques to remove contaminants from coal; assessment of the environmental consequences from the utilization of coal cleaning processes; and the development of control technology to avoid adverse discharge effects.
2. *Synthetic Fuels.* The assessment of the multimedia discharges and control technique development for technologies converting coal to gaseous, liquid, and refined solid fuels.

Both programs deal with the multimedia (air, water, and solid) discharge effects. However, the coal cleaning program has the additional responsibility to develop the basic processing technology. On the other hand, the synthetic fuel program only deals with the potential environmental effects and control technology. There is a direct interface of the two programs since characterizations of coal and physical coal processing are both involved in the conversion of coal to synthetic fuels.

The activities in the synthetic fuels program are divided into six major categories (figure 3):

1. *Environmental Assessment.* The identification and quantification of the multimedia discharges, and the potential health and ecological effects of these discharges.
2. *Control Technology Development.* Development of process modification and new control processes that would eliminate any adverse effects of these multimedia discharges.
3. *Special Studies.* Studies addressing particular problems and specific technologies.
4. *Bench Scale Facilities.* Integrated facilities to evaluate generic control systems, evaluations of modification/new technologies, and quantification of multimedia discharges.
5. *Pilot Plant Activities.* Evaluation of the composition and quantities of the multimedia emissions/discharges, their potential environmental effects, and effects of feedstock/process variations on the quality of discharges.
6. *Commercial Activities.* Evaluation of existing commercial operations as to emissions/discharges, efficiencies of control systems, and effects of plant variations.

Each environmental assessment contractor (figure 4) deals with a specific technology for converting coal to synthetic fuels and relates to one of the following categories:

1. Low-Btu Gasification,
2. High-Btu Gasification, and
3. Coal Liquefaction.

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The assessments are 3-year studies that will enable the contractor to develop into a center of expertise in each specific area and will address the following types of areas:

1. Background on current process technology,
2. Environmental data acquisition,
3. Current environmental background,
4. Control technology development, and
5. Environmental analysis/evaluation.

The control technology development contractors are the same type, and have the same rationale as the assessment contractors--that is, to develop centers of expertise. Both groups of contractors are responsible for broad technical input and guidance for the synthetic fuels program. However, the control technology contractors' responsibilities are structured differently than those in the environmental assessment area. The control technology contractors relate to specific sections of the conversion plant which will allow the maximum applicability of control development to the following three conversion technologies being addressed (figure 5):

1. *Converter Output Cleanup.* Process units that deal with the removal of undesirable contaminants from the raw gas or liquids.
2. *Products/Byproducts.* Process units that convert the cleaned gas or liquids into marketable products, and recovery of byproducts material, such as sulfur.
3. *Waste, Water, Fugitive Emissions.* Process technology that deals with broad multisource discharge streams.

The special studies activities address particular problem areas and/or technologies. These studies normally rely upon specific expertise or capabilities in various organizations. Figure 6 depicts the types of studies conducted in this area. These studies range from laboratory evaluations and bench scale process development to broad paper studies.

The bench scale facilities (figure 7) are based on research grants to identify problems, to evaluate generic control technology and new or modified control techniques. The Research Triangle Institute is conducting a comprehensive chemical analysis of the discharges from a small gasifier that can be operated in a nonisothermal mode. This study attempts to correlate operating parameter versus the composition of the off gases. The North Carolina State University will install a 22.5-kg/hr (50-lb/hr) gasifier capable of evaluating various raw gas cleanup techniques and various high and low temperature acid gas purification systems. The University of North Carolina is studying water treatment systems.

The pilot plant activities (figure 8) interface with various pilot plant operations in the private and Federal sectors. These activities vary from development of recommended test programs and procedures to sampling and analysis.

The commercial activities (figure 9) deal with data acquisition at operating commercial facilities to quantify the multimedia discharges and effects of process variations on the composition or quality of the discharges. The evaluation of the Kosovo Lurgi Gasification Plant in Yugoslavia is the largest and most comprehensive of these activities.

Details of these above programs will be dealt with during this symposium.

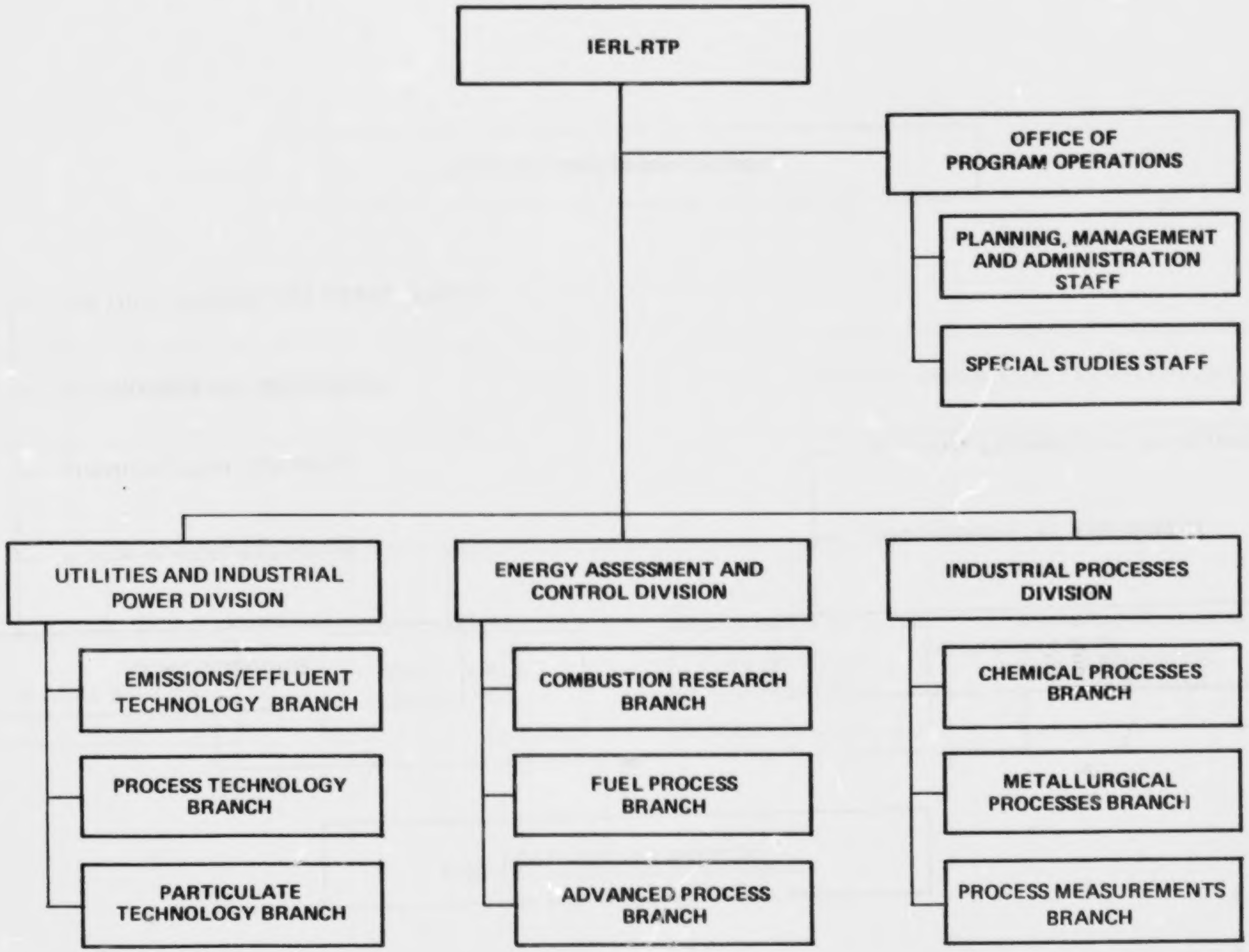
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Figure 1. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina.

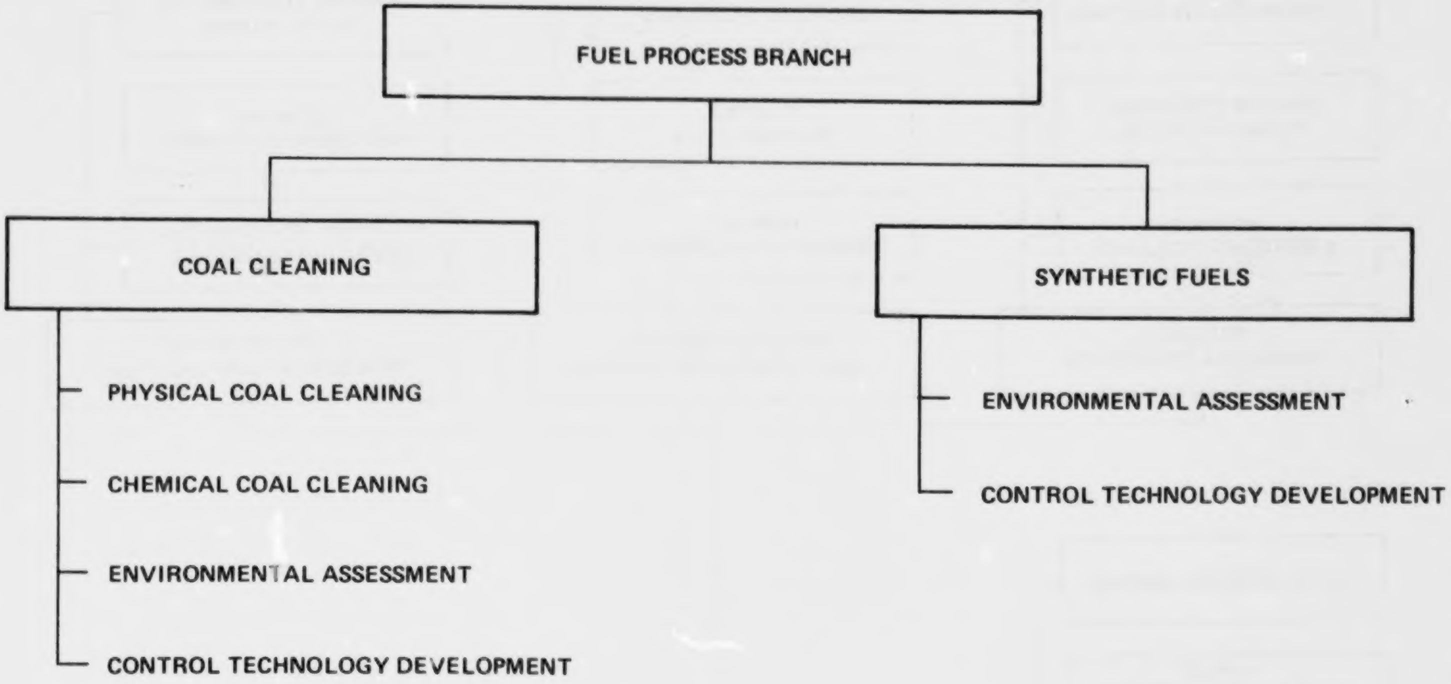
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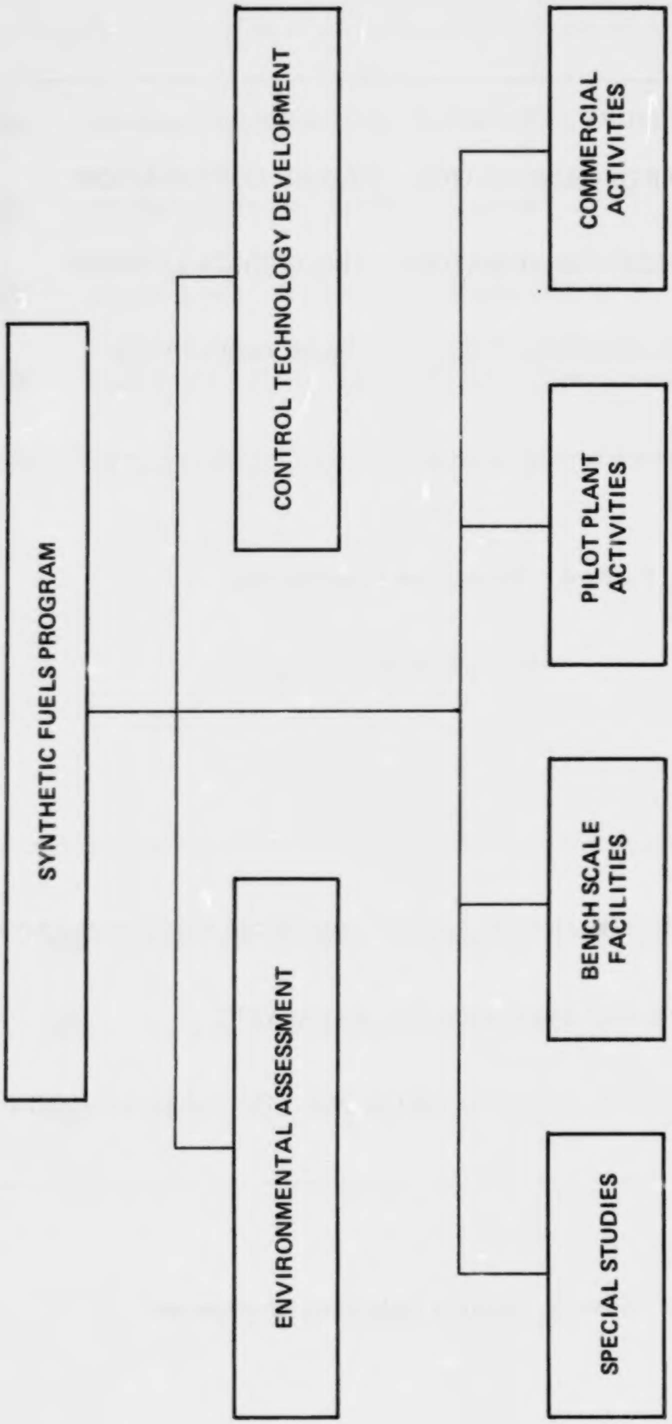
Figure 2. Fuel process branch.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ENVIRONMENTAL ASSESSMENT
CONTROL TECHNOLOGY DEVELOPMENT
SPECIAL STUDIES
BENCH SCALE FACILITIES
PILOT PLANT ACTIVITIES
COMMERCIAL ACTIVITIES

Figure 3. Synthetic fuels program.

- LOW-BTU GASIFICATION – RADIAN CORPORATION
- HIGH-BTU GASIFICATION – TRW ENERGY SYSTEMS
- COAL LIQUEFACTION – HITTMAN ASSOCIATES

Figure 4. Environmental assessment.

- CONVERTER OUTPUT CLEANUP – HYDROCARBON RESEARCH, INC.
- PRODUCTS AND BYPRODUCTS – CATALYTIC
- WASTE, WATER, FUGITIVE EMISSIONS – PULLMAN/KELLOGG

Figure 5. Control technology development.

◆ COMBINED CYCLES ENVIRONMENTAL PROBLEMS

◆ CONVERSION RESIDUES LEACHANT

◆ SYNTHETIC FUEL WATER REQUIREMENT

◆ ADVANCED FUEL CONTAMINANT REMOVAL CHEMISTRY

◆ DESULFURIZATION/DINITROGENATION OF LIQUIDS

Figure 6. Special studies.

◆ NONISOTHERMAL POLLUTANT IDENTIFICATION

◆ RAW AND ACID GAS CLEANUP FACILITIES

◆ WATER TREATMENT FACILITIES

Figure 7. Bench scale facilities.

- RILEY-STOKER
- ERDA INTERAGENCY
    - SOLVENT REFINED COAL
    - SLAGGING GASIFIER
    - WELLMAN GALUSHA

Figure 8. Pilot plant activities.

- KOSOVO LURGI GASIFICATION PLANT
- WILPUTTE GASIFIERS
- ERDA INDUSTRIAL GASIFIER DEMONSTRATIONS

Figure 9. Commercial activities.

ENVIRONMENTAL ASSESSMENT METHODOLOGY FOR FOSSIL ENERGY PROCESSES

by

R. P. Hangebrauck
Director, Energy Assessment and Control Division
Industrial Environmental Research Laboratory/RTP
Office of Energy, Minerals, and Industry
Environmental Protection Agency
Research Triangle Park,
North Carolina 27711

Abstract

IERL/RTP is conducting a number of programs involving environmental assessment and control technology development for both energy and industrial processes. However, this report focuses on one particular aspect; i.e., the status of some IERL/RTP efforts to develop Environmental Assessment Methodology, especially as it relates to the Federal Interagency Energy/Environment R&D Program.

For purposes of brevity in presentation of a large number of concepts relating to formulation of Environmental Assessment Methodology, this paper is formatted as a series of figures or tables which outline the essential features of Environmental Assessment Methodology being developed for fossil energy processes. It should be noted that the approaches indicated are developing and therefore subject to substantial change, but certain components are better established than others.

The efforts to develop Environmental Assessment Methodology involve several participating environmental assessment contractors who, as a part of their overall activities, have been assigned tasks to develop one or more of the specialized environmental assessment methodology components. The various components when complete will constitute the overall environmental assessment methodology protocol. This methodology is needed on a reasonably near-term basis to eliminate large gaps, inefficiencies and proliferation of techniques for evaluating or comparing environmental effectiveness. However, the potential value and usefulness of the approaches developed have such significance for the Agency that it would be undesirable to proceed in other than a logical and orderly fashion. An Environmental Assessment Steering Committee is in operation (see Appendix A for members) to support certain methodology tasks and provide review and consultation on others.

ACKNOWLEDGMENTS

The author acknowledges the direct input and/or availability of information developed by IERL/RTP personnel and their contractors, and personnel of other laboratories in EPA's Office of Research and Development.

SUMMARY AND CONCLUSIONS

Environmental assessment and control technology development programs are underway as part of the Interagency Energy/Environment R&D Program. The Industrial Environmental Research Laboratory at the Research Triangle Park, North Carolina, is conducting work in the fossil energy area in connection with this effort. The environmental assessment work underway is organized on an industry basis and provides for a multipollutant, multimedia analysis of problems and solutions in support of the standards setting and regulatory functions of EPA. Substantial need exists for environmental assessment methodology to support this rather ambitious undertaking.

This presentation outlines a number of the approaches or components comprising the environmental assessment methodologies. The approaches, because of their complexity in dealing totally with such entities as complex effluents, are only partially developed at this time. However, enough progress has been made to illustrate the overall approach and several facets which are important components. These include:

1. Gathering and analyzing of existing process data on energy systems.
2. Phased (Levels 1, 2, and 3) comprehensive chemical/biological testing of process effluents.
3. Techniques for defining when and which more costly detailed chemical analysis is needed.
4. Compiling and organizing information on control/disposal approaches.
5. Control assays to provide standardized laboratory procedures to be used in conjunction with Level 1 sampling and analysis to define the best potential control options.
6. Use of existing health and ecological effects and other data to define Multimedia Environmental Goals (MEG's).
7. Source analysis models to evaluate environmental alternatives by utilizing MEG's to determine potential degree-of-hazard or toxic unit discharge rate for a given control option or plant.
8. Formats for information to be included in standards of practice manuals which provide part of the research documentation from the Office of Research and Development as input to EPA's program offices. Such manuals will consist of an integrated, multimedia, industry-oriented, single-package review of the environmental requirements, guidelines, and best control/disposal options.

The methodologies being developed as a part of the environmental assessment program are of extreme importance to the Agency in that they represent prototype approaches to multimedia, multipollutant problem identification and control effectiveness evaluation for complex effluents. They are prototypes of potential future regulatory approaches that can handle the whole problem and are aimed at preventing problems before they occur. Hopefully they will allow resolution of existing problems on other than a one-pollutant-at-a-time basis, a basis which is fraught with endless studies, only partially effective results, and high cost at all levels of implementation.

ENVIRONMENTAL ASSESSMENT

- Current Process Technology Background
- Environmental Data Acquisition
- Current Environmental Background
- Environmental Objectives Development
- Control Technology Assessment
- Environmental Alternatives Analysis

CONTROL TECHNOLOGY DEVELOPMENT

- Gas Treatment
- Liquids Treatment
- Solids Treatment
- Final Disposal
- Process Modification
- Combustion Modifications
- Fuel Cleaning
- Fugitive Emissions Control
- Accidental Release Technology

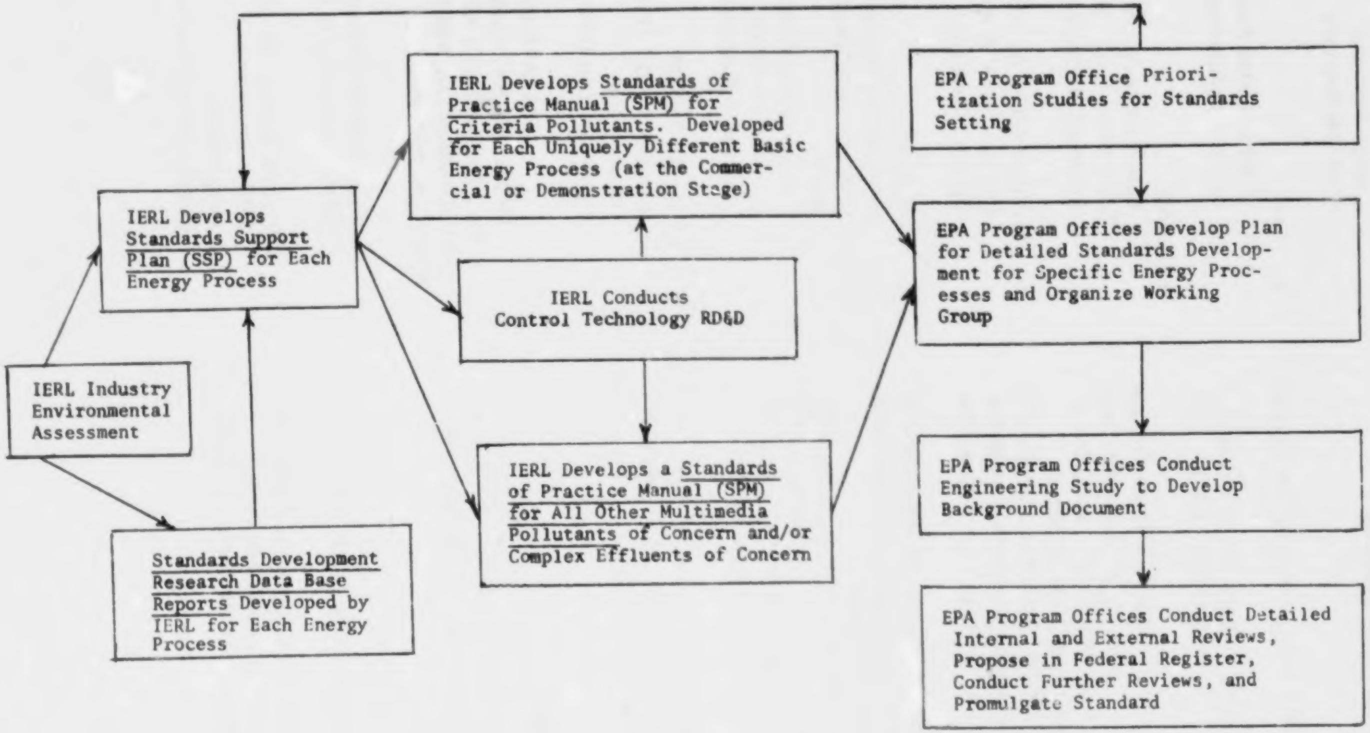
TECHNOLOGY AREAS

- Conventional Combustion
- Nitrogen Oxide/Combustion Modification Control
- Fluid Bed Combustion
- Advanced Oil Processing
- Coal Cleaning
- Synthetic Fuels

OUTPUT OBJECTIVES FOR ENVIRONMENTAL ASSESSMENT

- Defined Research Data Base for Standards
- Quantified Control R&D Needs
- Quantified Control Alternatives
- Quantified Media Degradation Alternatives
- Quantified Nonpollutant Effects and Siting Criteria Alternatives

IERL/RTP STANDARDS DEVELOPMENT SUPPORT R&D

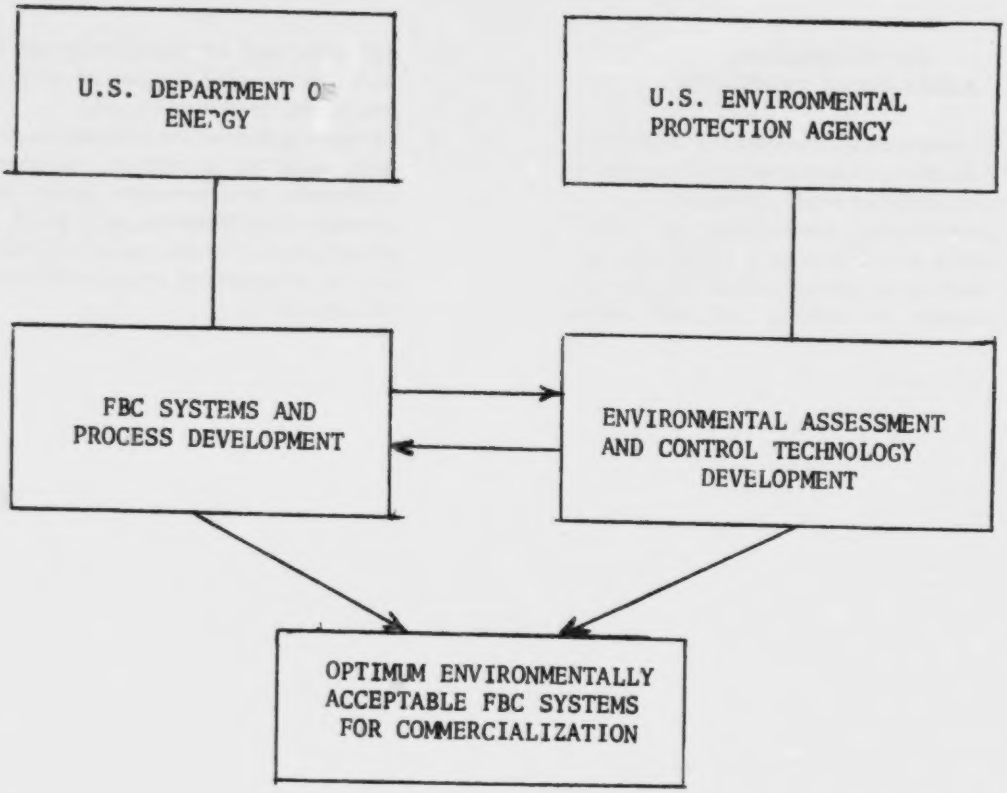

IERL Industry Environmental Assessment
IERL Develops Standards Support Plan (SSP) for Each Energy Process
Standards Development Research Data Base Reports Developed by IERL for Each Energy Process
IERL Develops Standards of Practice Manual (SPM) for Criteria Pollutants. Developed for Each Uniquely Different Basic Energy Process (at the Commercial or Demonstration Stage)
IERL Conducts Control Technology RD&D
IERL Develops a Standards of Practice Manual (SPM) for All Other Multimedia Pollutants of Concern and/or Complex Effluents of Concern
EPA Program Office Prioritization Studies for Standards Setting
EPA Program Offices Develop Plan for Detailed Standards Development for Specific Energy Processes and Organize Working Group
EPA Program Offices Conduct Engineering Study to Develop Background Document
EPA Program Offices Conduct Detailed Internal and External Reviews, Propose in Federal Register, Conduct Further Reviews, and Promulgate Standard

PRIMARY USERS OF PROGRAM ACTIVITIES/RESULTS

- EPA
  - IERL/RTP (several inputs to internal program)
  - OEMI/OR&D (inputs for planning, integrated assessments, OMB, Congress)
  - Health and Ecological Effects Groups (samples, source characterization, ecological testing needs, pollutant effects data needs, test facilities)
  - Environmental Sciences (analytical needs, pollutant transport/transformation study needs, test facilities, samples)
  - Policy and Planning (development of basis for technology/environmental alternatives and costs)
  - Regional Offices (information on problems and control options on a multimedia basis; technical assistance)
  - Enforcement (control information)
  - Control Technology Recommendations
  - Design Reviews
  - Proposal Reviews
- STATE AND LOCAL REGULATORY
  - Multimedia integration of industry environmental considerations
- NIOSH
  - Information
  - Samples
  - Sharing of Data Acquisition Burden
  - Common Control Technology Identification
- DOE
  - Environmental Input to On-going Program
  - Independent Environmental Review of DOE's Technology Development
  - Environmental Assessment Methodology
- FEA
  - Energy Related Aspects of Environmental Control Approaches
- NAS
  - Environmental Inputs to National Academy of Sciences/National Academy of Engineering Studies
- ENVIRONMENTAL GROUPS
  - Environmental Alternatives and Control Option Information
- INDUSTRY
  - Process Developers
  - Control Technology Developers/Suppliers
  - Environmental Engineers/Consultants
  - Coal and Oil Processors/Users
  - Equipment Suppliers/Servicers
- GENERAL PUBLIC
  - Guidelines for Direct Use of Individuals
  - Information on Problems/Control

STATE OF DEVELOPMENT/COMMERCIALIZATION AFFECTS APPROACH TO ENVIRONMENTAL ASSESSMENT AND CONTROL TECHNOLOGY DEVELOPMENT

- Existing Energy Technologies
  - Commercial/Private Sector Capacity
- Emerging Energy Technologies
  - ERDA/Department of Energy Developments
  - Private Sector Developments


U.S. DEPARTMENT OF ENERGY
U.S. ENVIRONMENTAL PROTECTION AGENCY
FBC SYSTEMS AND PROCESS DEVELOPMENT
ENVIRONMENTAL ASSESSMENT AND CONTROL TECHNOLOGY DEVELOPMENT
OPTIMUM ENVIRONMENTALLY ACCEPTABLE FBC SYSTEMS FOR COMMERCIALIZATION

EMERGING TECHNOLOGIES--PARALLEL EFFORTS IN PROCESS DEVELOPMENT AND ENVIRONMENTAL ASSESSMENT

(Example for Fluidized Bed Combustion)*

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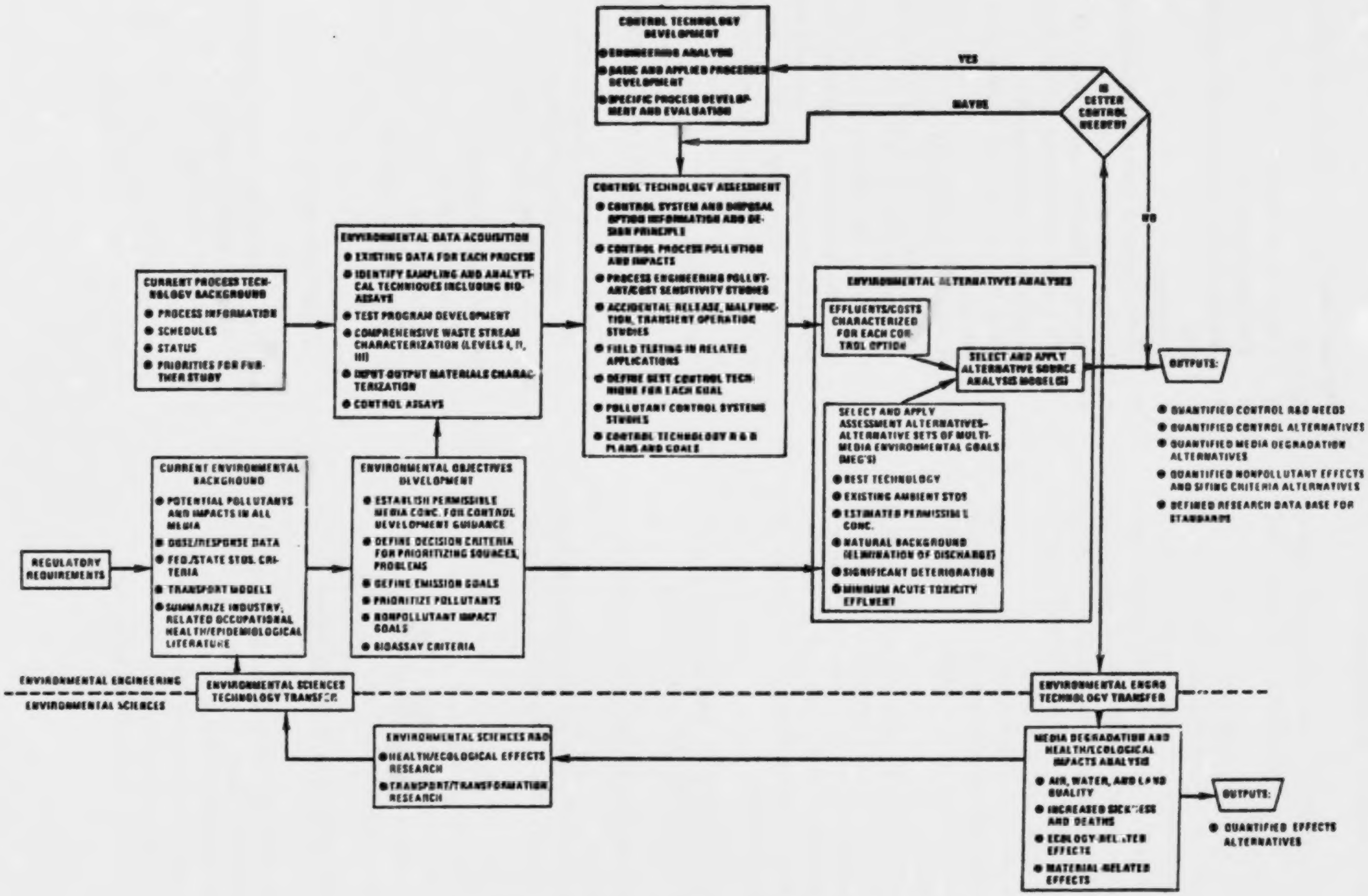
*Ref. Murthy, K. and H. Nack, "Progress in EPA's Fluidized Bed Combustion Environmental Assessment and Control Technology Development Program," Presented at the Fluidized-Bed Combustion Technology Workshop, Reston, Virginia (April 1977).

ENVIRONMENTAL ASSESSMENT DEFINITION

An environmental assessment, as defined for IERL/RTP studies of fossil energy processes, is a continuing iterative study aimed at:

1. Determining comprehensive multimedia environmental loadings and environmental control costs, from the application of existing and best future definable sets of control/disposal options, to a particular set of sources, processes, or industries; and
2. Comparing the nature of these loadings with existing standards, estimated multimedia environmental goals, and bioassay specifications as a basis for prioritization of problems/control needs and for judgment of environmental effectiveness.


CURRENT PROCESS TECHNOLOGY BACKGROUND
● PROCESS INFORMATION
● SCHEDULES
● STATUS
● PRIORITIES FOR FURTHER STUDY
ENVIRONMENTAL DATA ACQUISITION
● EXISTING DATA FOR EACH PROCESS
● IDENTIFY SAMPLING AND ANALYTICAL TECHNIQUES INCLUDING BIOASSAYS
● TEST PROGRAM DEVELOPMENT
● COMPREHENSIVE WASTE STREAM CHARACTERIZATION (LEVELS I, II, III)
● INPUT-OUTPUT MATERIALS CHARACTERIZATION
● CONTROL ASSAYS
CONTROL TECHNOLOGY DEVELOPMENT
● ENGINEERING ANALYSIS
● BASIC AND APPLIED PROCESSES DEVELOPMENT
● SPECIFIC PROCESS DEVELOPMENT AND EVALUATION
CONTROL TECHNOLOGY ASSESSMENT
● CONTROL SYSTEM AND DISPOSAL OPTION INFORMATION AND DESIGN PRINCIPLE
● CONTROL PROCESS POLLUTION AND IMPACTS
● PROCESS ENGINEERING POLLUTANT/COST SENSITIVITY STUDIES
● ACCIDENTAL RELEASE, MALFUNCTION, TRANSIENT OPERATION STUDIES
● FIELD TESTING IN RELATED APPLICATIONS
● DEFINE BEST CONTROL TECHNIQUE FOR EACH GOAL
● POLLUTANT CONTROL SYSTEMS STUDIES
● CONTROL TECHNOLOGY R & D PLANS AND GOALS
YES
MAYBE
IS BETTER CONTROL NEEDED?
NO
ENVIRONMENTAL ALTERNATIVES ANALYSES
EFFLUENTS/COSTS CHARACTERIZED FOR EACH CONTROL OPTION
SELECT AND APPLY ALTERNATIVE SOURCE ANALYSIS MODEL(S)
SELECT AND APPLY ASSESSMENT ALTERNATIVES-ALTERNATIVE SETS OF MULTIMEDIA ENVIRONMENTAL GOALS (MEG'S)
● BEST TECHNOLOGY
● EXISTING AMBIENT STDS
● ESTIMATED PERMISSIBLE CONC.
● NATURAL BACKGROUND (ELIMINATION OF DISCHARGE)
● SIGNIFICANT DETERIORATION
● MINIMUM ACUTE TOXICITY EFFLUENT
OUTPUTS:
● QUANTIFIED CONTROL R&D NEEDS
● QUANTIFIED CONTROL ALTERNATIVES
● QUANTIFIED MEDIA DEGRADATION ALTERNATIVES
● QUANTIFIED NONPOLLUTANT EFFECTS AND SITING CRITERIA ALTERNATIVES
● DEFINED RESEARCH DATA BASE FOR STANDARDS
REGULATORY REQUIREMENTS
CURRENT ENVIRONMENTAL BACKGROUND
● POTENTIAL POLLUTANTS AND IMPACTS IN ALL MEDIA
● DOSE/RESPONSE DATA
● FED./STATE STDS. CRITERIA
● TRANSPORT MODELS
● SUMMARIZE INDUSTRY; RELATED OCCUPATIONAL HEALTH/EPIDEMIOLOGICAL LITERATURE
ENVIRONMENTAL OBJECTIVES DEVELOPMENT
● ESTABLISH PERMISSIBLE MEDIA CONC. FOR CONTROL DEVELOPMENT GUIDANCE
● DEFINE DECISION CRITERIA FOR PRIORITIZING SOURCES, PROBLEMS
● DEFINE EMISSION GOALS
● PRIORITIZE POLLUTANTS
● NONPOLLUTANT IMPACT GOALS
● BIOASSAY CRITERIA
ENVIRONMENTAL ENGINEERING
ENVIRONMENTAL SCIENCES
ENVIRONMENTAL SCIENCES TECHNOLOGY TRANSFER
ENVIRONMENTAL SCIENCES R&D
● HEALTH/ECOLOGICAL EFFECTS RESEARCH
● TRANSPORT/TRANSFORMATION RESEARCH
ENVIRONMENTAL ENGRG TECHNOLOGY TRANSFER
MEDIA DEGRADATION AND HEALTH/ECOLOGICAL IMPACTS ANALYSIS
● AIR, WATER, AND LAND QUALITY
● INCREASED SICKNESS AND DEATHS
● ECOLOGY-RELATED EFFECTS
● MATERIAL-RELATED EFFECTS
OUTPUTS:
● QUANTIFIED EFFECTS ALTERNATIVES

Environmental assessment/control technology development diagram.

ENVIRONMENTAL ASSESSMENTS SERVE AS PARTIAL INPUT TO INTEGRATED ASSESSMENTS

- The Purpose of the Integrated Assessment for Coal-Based Energy Technologies Is:
  - To identify, describe, compare, and quantify where possible the range and magnitude of biophysical, socioeconomic, and energy impacts of alternative mixes, rates, levels, and timing of the development and deployment of coal-based energy technologies, supply systems, and end uses.
  - To identify and comparatively analyze technological and institutional methods of avoiding or mitigating undesirable impacts.
  - To recommend alternative policies that will achieve the best balance of environmental quality, energy efficiency, economic costs, and social benefits and to propose strategies for policy implementation.

GENERAL STATUS OF ENVIRONMENTAL ASSESSMENT METHODOLOGY

- Developing (partly established, partly conceptual)
- Environmental Assessment Methodology assignments made to specific E. A. contractors
- Because of timing, methodology developed in parallel with preliminary environmental assessment
- First compilation of methodology to be available near end of 1977.

ENVIRONMENTAL ASSESSMENT

- Current Process Technology Background
- Environmental Data Acquisition
- Current Environmental Background
- Environmental Objectives Development
- Control Technology Assessment
- Environmental Alternatives Analysis

CURRENT PROCESS TECHNOLOGY BACKGROUND

Process Assessment Criteria include such factors as:

- Commercial status
- Existing capacity
- Schedules for construction, development, etc.
- Priorities
- Quantities and types of residual emissions
- Projected process costs
- Energy efficiency and form of energy. (This was considered a cost factor with independent significance.)
- Applicability; i.e., the extent of projected markets
- Rate of availability; i.e., how fast technology can be brought to commercial availability and applied
- Probability of success in development (includes a variety of considerations; e.g., the scale on which the process has been operated; the magnitude of the investment for commercial plants; how it will fare in the competition among technologies)

ENVIRONMENTAL DATA ACQUISITION

Unit Operations Organization for Study of Pollutant Sources (Examples)

- Raw Material Storage
  - Windblown dusts
  - Water runoff
  - Leakage and venting

- Transportation
  - Windblown dusts
  - Open conveyor
  - Transport liquids (water, organics)
  - Other handling losses
  - Vehicular transport

- Raw Material Preparation
  - Fuel or raw material drying

  - Grinding, pulverization
  - Particulate collectors
  - Coal washing
  - Pretreatment steps
  - Vents

- Reactors/Convertors/Combustors
  - Raw material feed mechanism
  - Chemical/physical transformations
  - Leakage and venting
  - Flue gas from combustion/power steam generation from fuel or fuel residues
  - Product utilization

- Process Stream Separation/Cleaning/Treatment
  - Raw gas cleanup
  - Gas purification systems
  - Catalyst/sorbent regeneration
  - Claus sulfur plant tail gas treatment
  - Flue gas desulfurization units
  - Vents and flares
  - Particulate collectors
  - Tar oil/water separators
  - Waste water treatment
  - Leaks
  - Cleaning agents and additives

- Products and By-Products
  - Product upgrading and recovery
  - Sulfur and other by-product recovery
  - Handling and storage losses
  - Utilization

- Final Disposal
  - Flyash, ash, and slag
  - Spent catalyst and sorbent disposal
  - Hazardous solid wastes
  - Ponds
  - Landfills
  - Piles
  - Thermal cooling (air, water, heat, cooling water, blowdown, drift)

- Auxiliary Facilities
  - Oxygen plant
  - Hydrogen plant

- Accidental/Transient Release

ENVIRONMENTAL DATA ACQUISITION

A phased approach:

Level 1 - *Comprehensive Screening* ("Criteria pollutants" included)

Level 2 - Directed *Detailed Analysis* Based on Level 1

Level 3 - *Process Monitoring on Selected Priority Pollutants* Based on Levels 1 and 2

ENVIRONMENTAL DATA ACQUISITION

Level 1 Sampling and Analysis

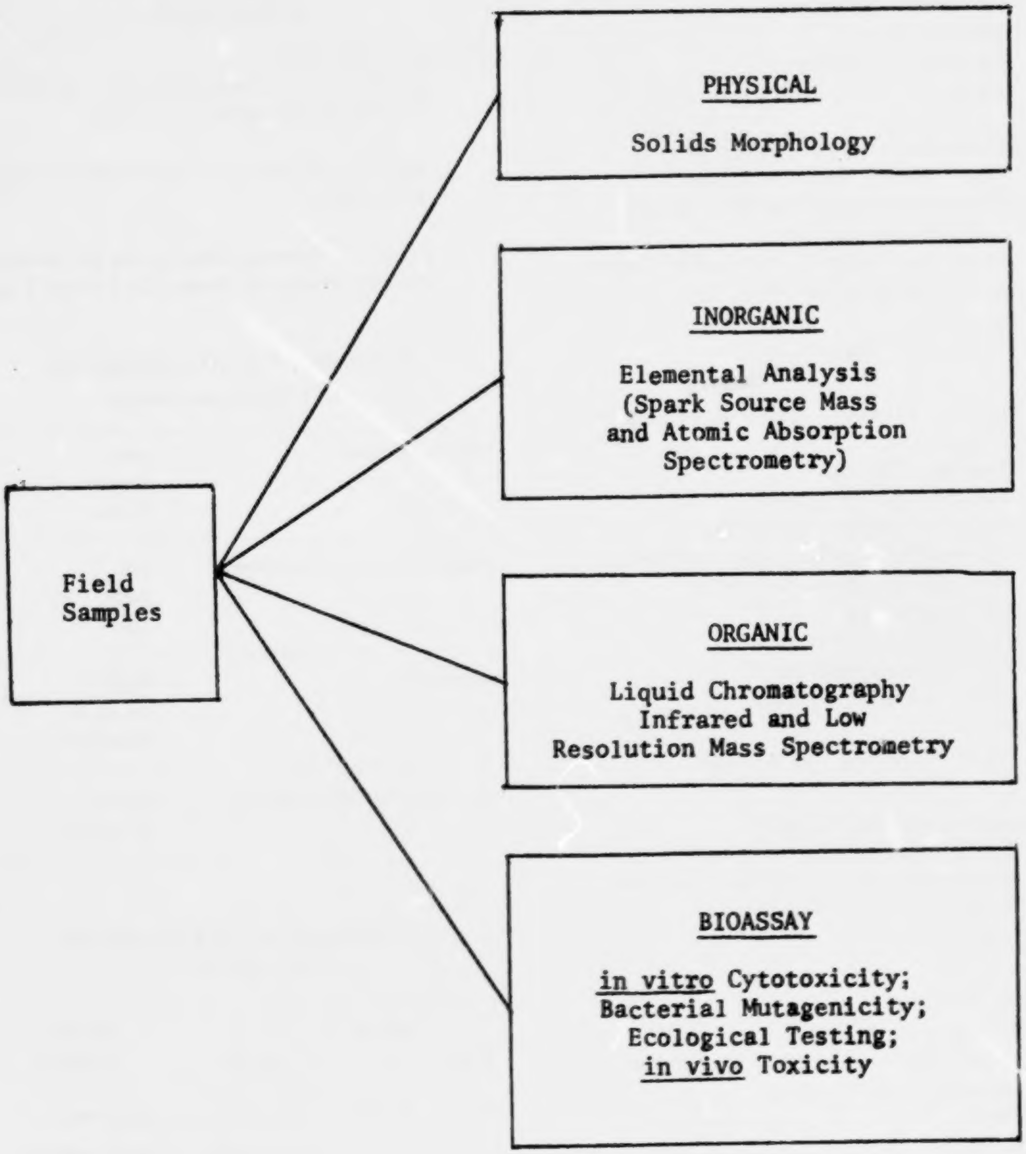
Effluent Samples:	**Gases** **Liquids** **Solids**
Evaluated for Discharge to Media:	**Air** **Water** **Land**
Analyses:	**Physical** **Chemical** **Biological**
Key Environmental Parameters:	**Health** **Ecological**

ENVIRONMENTAL DATA ACQUISITION

Level 1 Sampling*

Stream	Sample size	Location	Sampling procedure
Gas	30 m^3	Ducts, stacks	SASS train
Liquid	10 l	Lines or tanks	Tap or valve sampling
		Open free-flowing streams	Dipper method
Solids	1 kg	Storage piles	Coring
		Conveyors	Full stream cut

* Environmental Assessment Sampling and Analysis: Phased Approach and Techniques for Level 1, EPA-600/2-77-115 (NTIS No. PB 268563/AS), June 1977.


PHYSICAL
Solids Morphology
INORGANIC
Elemental Analysis (Spark Source Mass and Atomic Absorption Spectrometry)
Field Samples
ORGANIC
Liquid Chromatography Infrared and Low Resolution Mass Spectrometry
BIOASSAY
in vitro Cytotoxicity; Bacterial Mutagenicity; Ecological Testing; in vivo Toxicity

LEVEL 1 ANALYSIS*

*Environmental Assessment Sampling and Analysis: Phased Approach and Techniques for Level 1, EPA-600/2-77-115 (NTIS No. PB 268563/AS), June 1977.

ENVIRONMENTAL DATA ACQUISITION
DRAFT BIOASSAY PROTOCOLS*

LEVEL 1 - MINIMAL TEST MATRIX

Sample Type	Health Effects Tests			Ecology Effects Tests		
Water and Liquids	Microbial Mutagenesis	Rodent Acute Toxicity		Algal Bioassay	Static Bioassays	Soil Microcosm
Solids (Aqueous Extract, Feed, Product, Waste)	Microbial Mutagenesis	Rodent Acute Toxicity		Algal Bioassay	Static Bioassays	Soil Microcosm
Gases (Grab Sample)						Plant Stress Ethylene
Particulates	Microbial Mutagenesis	(Rodent Acute Toxicity)**	Cyto-toxicity			Soil Microcosm
Sorbent (Extract)	Microbial Mutagenesis		Cyto-toxicity			

*IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Biological Tests for Pilot Studies, EPA-600/7-77-043 (NTIS No. PB 268484/AS) April 1977.

**Recommended test not specified because of limited sample availability of secondary priority.

LEVEL 1 - BIOASSAY TESTS ORGANISMS

Health Effects Tests

- Microbial Mutagenesis
  - Salmonella typhimurium

- Cytotoxicity
  - Rabbit Alveolar Macrophages (RAM)
  - Human Lung Embryo Fibroblasts (WI-38)

- Rodent Acute Toxicity
  - Rats

Ecological Effects Tests

Fresh Water

- Algae Bioassay
  - Selenastrum capricornutum
  - Microcystis aeruginosa
  - Amacystis cyanea
  - Anabaena fos-Aquae
  - Diatom-Cyclotella
  - Diatom-Nitzschia

- Static Bioassay
  - Fathead minnow
  - Daphnia pulex

Marine

- Marine Algae Bioassay
  - Skeletonema costatum

- Static Bioassay
  - Juvenile sheepshead minnows (cyprinodon variegatus)
  - Adult grass shrimp (Palaemonetes pugio or P. vulgaris)

Terrestrial

- Plant Stress Ethylene Test
  - Soybean

- Soil-Litter Microcosm
  - Soil organisms

ENVIRONMENTAL ASSESSMENT MEASUREMENT AND EVALUATION SUMMARY

Environmental Assessment Measurement Levels	Sampling	Analysis					Environmental Alternatives Analysis			
		Chemical		Bioassay						
	Accuracy	Accuracy/ Specificity	Conc. Level Measured	Accuracy/ Specificity	Effect Level Measured	Media Measured	Assessment Alternatives (Multimedia Environ. Goal Sets Used)	Source Analysis Models Used	Media Evaluated	Effect Level Evaluated
Level 1 (Comprehensive Screening)	Low	Low	Effluent	Low	Acute Exposure	Effluent	MATE*	SAM/IA	Effluent	Acute Exposure
Level 2 (Directed Detailed Analysis Based on Level 1)	Higher	Higher	Effluent	Higher	Acute Exposure	Effluent	MATE* (EPC** ES***)	SAM/IA SAM/I SAM/II	Effluent (Est. Ambient)	Acute Exposure Chronic Exposure
Level 3 (Process Measurements on Selected Priority Pollutants Based on Levels 1 and 2)	Highest	Highest	Effluent	Highest	Chronic Exposure	Effluent	(EPC** ES***)	SAM/II	(Est. Ambient)	Chronic Exposure

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* MATE (Minimum Acute Toxicity Effluent)
** EPC (Estimated Permissible Concentrations)
*** ES (Existing Standards)

ANALYTICAL CHEMICAL TECHNIQUES APPLICABLE IN LEVEL 2 FOLLOWING LEVEL 1 SURVEY OF STREAM CONTENTS*

Category A

Wet Chemical Methods

(e.g., SO_4, NO_3, F, total phenolics)

Elemental Analysis

Spark-Source Mass Spectrometry

Atomic Absorption Spectrometry

Arc and Spark Emission Spectrometry

Neutron Activation Analyses

X-Ray Fluorescence

Organic Materials

Infrared Spectrometry

G.C. - Mass Selective Detector

G.C. - Selective Detector
(e.g., Flame Ionization, Flame Emission, Electron Capture)

Chemi-Ionization Mass Spectrometry

Category B

Separation Techniques

High-Performance Liquid Chromatography

Gas Chromatography

Ion Exchange

Solvent Extraction

Structure Elucidation

Nuclear Magnetic Resonance

High-Resolution Mass Spectrometry

Photoelectron/Inner Shell Electron Spectrometry (Surface Inorganics)

Infrared Spectrometry

Quantitative Measurement

If not achieved in Separation or Structure Elucidation, utilize Category A.

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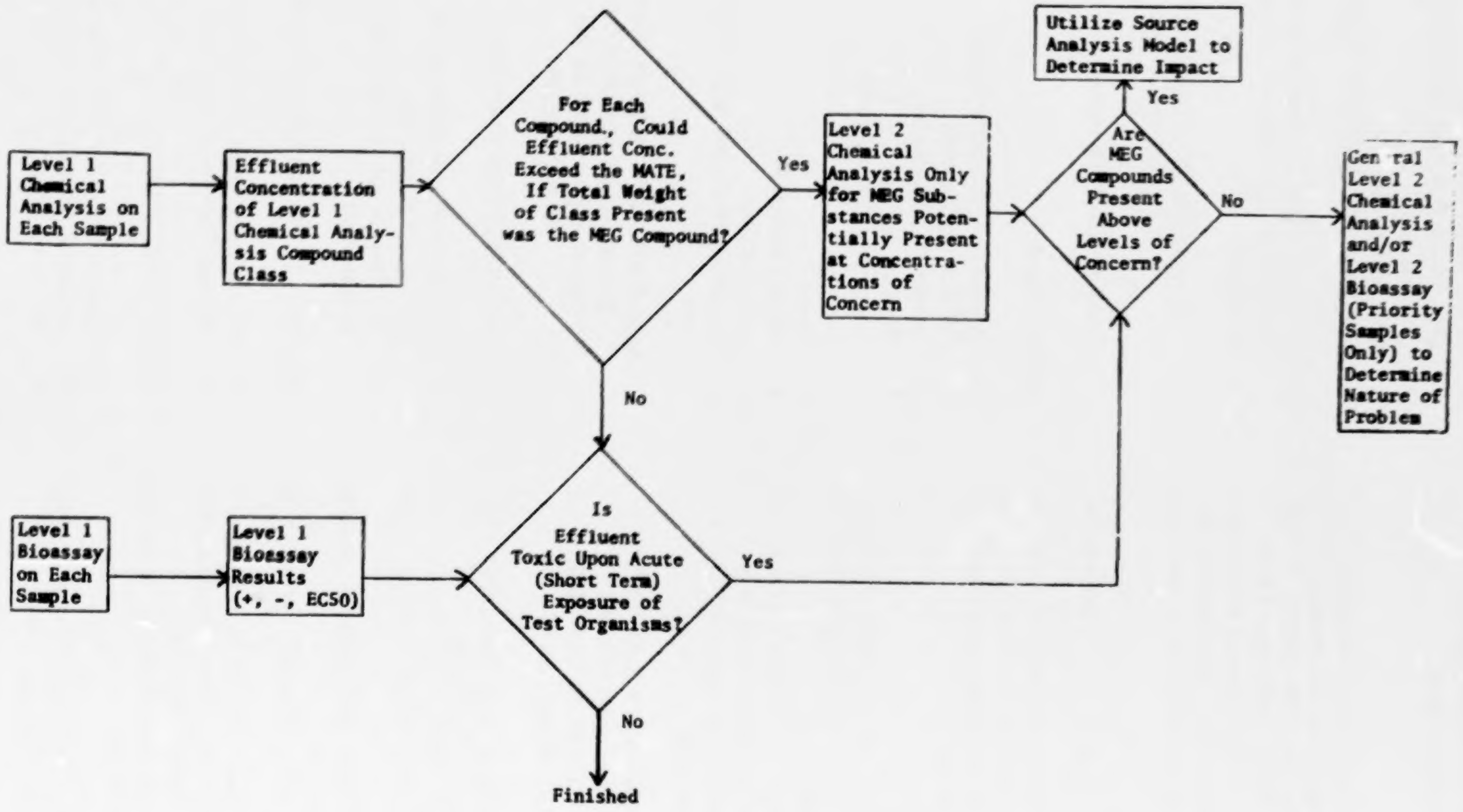
*This is not an all inclusive or an exclusive list. Choice of the most cost/information effective methods will vary from sample to sample. Environmental Assessment Sampling and Analysis: Phased Approach and Techniques for Level 1, EPA-600/2-77-115 (NTIS No. PB 268563/AS), June 1977.


Level 1 Chemical Analysis on Each Sample
Effluent Concentration of Level 1 Chemical Analysis Compound Class
For Each Compound., Could Effluent Conc. Exceed the MATE, If Total Weight of Class Present was the MEG Compound?
Yes
No
Level 2 Chemical Analysis Only for MEG Substances Potentially Present at Concentrations of Concern
Are MEG Compounds Present Above Levels of Concern?
Yes
Utilize Source Analysis Model to Determine Impact
No
General Level 2 Chemical Analysis and/or Level 2 Bioassay (Priority Samples Only) to Determine Nature of Problem
Level 1 Bioassay on Each Sample
Level 1 Bioassay Results (+, -, EC50)
Is Effluent Toxic Upon Acute (Short Term) Exposure of Test Organisms?
Yes
No
Finished

DECISION LOGIC FOR PHASED LEVEL 1-LEVEL 2 ANALYSIS

CURRENT ENVIRONMENTAL BACKGROUND

- REPORTS
  - Potentially Hazardous Emissions from the Extraction and Processing of Coal and Oil (Battelle) (EPA-650/2-75-038, NTIS No. PB 241803, May 1975)
  - Summary of Key Federal Regulations and Criteria for Multimedia Environmental Control (RTI) (Draft, June 1977)
  - Estimation of Permissible Concentrations of Pollutants for Continuous Exposure (RTI) (EPA-600/2-76-155, NTIS No. PB 253959/AS, June 1976)
  - Preliminary Format for Compilation of Ambient Trace Substances Data (RTI) (August 1976)

- ACTIVITIES
  - Compilation of Existing Physical, Chemical, and Toxicological Data for Specific Pollutants
  - Gathering of Information on Transport/Transformation Models
  - Compilation of Ambient Trace Substances Data

FEDERAL REGULATIONS APPLYING QUANTITATIVE LIMITATIONS TO SPECIFIC, POTENTIAL ENVIRONMENTAL POLLUTANTS

- National Primary and Secondary Ambient Air Quality Standards
- Occupational Safety and Health Administration Standards for Air Contaminants
- National Emission Standards for Hazardous Air Pollutants
- New Stationary Source Performance Standards
- Emissions Standards for Control of Air Pollution from New Motor Vehicles and New Motor Vehicle Engines
- National Interim Primary Drinking Water Regulations

Supplement: 1962 Public Health Service Regulations on Drinking Water

- EPA Effluent Standards
- EPA Toxic Pollutant Effluent Standards (Proposed)
- EPA Pesticide Limits
- Standards for Protection Against Radiation
- Criteria for the Evaluation of Permit Applications for Ocean Dumping of Materials

ENVIRONMENTAL OBJECTIVES DEVELOPMENT

(Multimedia Environmental Goals)

General Classes

- Organic and Inorganic Totals
- Organic Compounds
- Inorganic Compounds
- Physical Agents
- Complex Effluent Assays
- Heat
- Noise
- Microorganisms
- Radionuclides
- Nonpollutant Factor (e.g., water use, land use)

SELECTION FACTORS FOR CHOICE OF CHEMICAL SUBSTANCES AND PHYSICAL AGENTS TO BE INCLUDED IN MEG CHART

PRIMARY SELECTION FACTORS

- Known or Suspected as an Emission from Coal or Oil Processing
- All Classes of Compounds/Substances Represented

SECONDARY SELECTION FACTORS

- Found as Pollutant in the Environment
- Highest Toxicity

PRIORITIZING FACTORS

- Standards or Criteria Proposed or Set (Ambient, Emission, or Occupational)
- TLV or LD_{50} Known

- On EPA Ordered NIOSH Carcinogen List
- On EPA Consent Decree List

Approximate makeup of organic and inorganic categories and classes of substances on the list thus far:

	Categories	Classes	Substances
Organics Portion	26	45	350
Inorganics Portion	59	--	300
	85	45	650

MULTIMEDIA POTENTIAL POLLUTANT LIST

ORGANIC-COMPOUND CATEGORIES AND CLASSES

Category	Class
1 - Aliphatic Hydrocarbons	Alkanes and Cyclic Alkanes
	Alkenes, Cyclic Alkenes, and Dienes
	Alkynes
2 - Alkyl Halides	Saturated Alkyl Halides
	Unsaturated Alkyl Halides
3 - Ethers	Ethers
4 - Halogenated Ethers	Halogenated Ethers
5 - Alcohols	Primary Alcohols
	Secondary Alcohols
	Tertiary Alcohols
6 - Glycols, Epoxides	Glycols
	Epoxides
7 - Aldehydes, Ketones	Aldehydes, Ketones
8 - Carboxylic Acids & Derivatives	Carboxylic Acids with Additional Function Groups
	Amides
	Esters
9 - Nitriles	Nitriles
10 - Amines	Primary Amines
	Secondary Amines
	Tertiary Amines
11 - Azo Compounds, Hydrazine, & Deriv.	Azo Compounds, Hydrazine, & Deriv.
12 - Nitrosamines	Nitrosamines
13 - Mercaptans, Sulfides & Disulfides	Mercaptans
	Sulfides, Disulfides
14 - Sulfonic Acides, Sulfoxides	Sulfonic Acids
	Sulfoxides
15 - Benzene, Substituted Benzene Hydrocarbons	Benzene, Substituted Benzene Hydrocarbons
16 - Halogenated Aromatic Hydrocarbons	Halogenated Aromatic Hydrocarbons
17 - Aromatic Nitro Compounds	Aromatic Nitro Compounds
18 - Phenols	Monohydrics
	Dihydrics, Polyhydrics
	Hydroxy Compounds with Fused Rings
19 - Halophenols	Halophenols
20 - Nitrophenols	Nitrophenols
21 - Fused Aromatic Hydrocarbons & Derivatives	Fused Aromatic Hydrocarbons & Derivatives
22 - Fused Non-Alternant Polycyclic Hydrocarbons	Fused Non-Alternant Polycyclic Hydrocarbons
23 - Heterocyclic Nitrogen Compounds	Pyridine & Substituted Pyridines
	Fused 6-membered Ring Heterocycles
	Pyrrole & Fused Ring Derivatives of Pyrrole
	Nitrogen Heterocycles Containing Additional Hetero Atoms
24 - Heterocyclic Oxygen Compounds	Heterocyclic Oxygen Compounds
25 - Heterocyclic Sulfur Compounds	Heterocyclic Sulfur Compounds
26 - Organometallics	Alkyl or Aryl Organometallics
	Sandwich Type Organometallics
	Metal Porphyrins & Other Chelates

MULTIMEDIA POTENTIAL POLLUTANT LIST

INORGANIC CATEGORIES

(Element category includes zero valence species, ions of the element, and certain specific compounds)

Group		Category
IA	-	27 - Lithium
		28 - Sodium
		29 - Potassium
		30 - Rubidium
		31 - Cesium
IIA	-	32 - Beryllium
		33 - Magnesium
		34 - Calcium
		35 - Strontium
		36 - Barium
IIIA	-	37 - Boron
		38 - Aluminum
		39 - Gallium
		40 - Indium
		41 - Thallium
IVA	-	42 - Carbon
		43 - Silicon
		44 - Germanium
		45 - Tin
		46 - Lead
VA	-	47 - Nitrogen
		48 - Phosphorus
		49 - Arsenic
		50 - Antimony
		51 - Bismuth
VIA	-	52 - Oxygen
		53 - Sulfur
		54 - Selenium
		55 - Tellurium
VIIA	-	56 - Fluorine
		57 - Chlorine
		58 - Bromine
		59 - Iodine
IIIB	-	60 - Scandium
		61 - Yttrium
IVB	-	62 - Titanium
		63 - Zirconium
		64 - Hafnium
VB	-	65 - Vanadium
		66 - Niobium
		67 - Tantalum
VIB	-	68 - Chromium
		69 - Molybdenum
		70 - Tungsten
VIIB	-	71 - Maganese
VIII	-	72 - Iron
		73 - Ruthenium
		74 - Cobalt
		75 - Rhodium
		76 - Nickel
		77 - Platinum
IB	-	78 - Copper
		79 - Silver
		80 - Gold
IIB	-	81 - Zinc
		82 - Cadmium
		83 - Mercury
		84 - Lathanides
		85 - Actinides

MULTIMEDIA ENVIRONMENTAL GOALS

Emission Level Goals

	Based on Best Technology		Based on Ambient Factors				
	Existing Standards	Developing Technology	Minimum Acute Toxicity Effluent		Ambient Level Goal		Elimination of Discharge
	NSPS, BPT, BAT	Engineering Estimates (R&D Goals)	Based on Health Effects	Based on Ecological Effects	Based on Health Effects	Based on Ecological Effects	Natural Background
AIR WATER LAND							

Ambient Level Goals

	Current or Proposed Ambient Standards or Criteria		Toxicity Based on Estimated Permissible Concentration		Zero Threshold Pollutants Estimated on Permissible Concentrations
	Based on Health Effects	Based on Ecological Effects	Based on Health Effects	Based on Ecological Effects	Based on Health Effects
AIR WATER LAND					

CATEGORY: 15

WLN: R

BENZENE: C_6H_6 (benzol, phenylhydride, phene).
A clear, colorless liquid.

STRUCTURE:

PROPERTIES:

Molecular wt: 78.11; mp: 5.5; bp: 80.1;
d: 0.87865_4^{20}; vap. press: 100 mm at 26.1° C; vap. d: 2.77;
solubility in water: 1,780 mg/ℓ at 25° (ref. 52); soluble in tissue lipids.

NATURAL OCCURRENCE, CHARACTERISTICS, ASSOCIATED COMPOUNDS:

Benzene occurs in straight-run petroleum distillates and in coal-tar distillates. Rural background for benzene is reported as 0.1 ppbc (ref. 1). This is equivalent to 0.017 ppb or 0.054 $\mu g/m^3$. The odor recognition level is 10.5 to 210 mg/m^3 (ref. 3). Benzene participates to a very limited degree in photooxidation reactions (ref. 3). Benzene has been identified in at least one drinking water supply in the United States in concentrations as high as 10 μg/ℓ (ref. 13). There is a strong indication that plants may perform a major role in the degradation and synthesis of benzene in the environment (ref. 52).

TOXIC PROPERTIES, HEALTH EFFECTS:

Benzene is an acute and chronic poison. It is absorbed through the skin, but most often poisoning occurs through inhalation. The rate of absorption of benzene through the skin has been reported to be 0.4 $mg/cm^2/hr$ (ref. 53). It is estimated that 50 percent to 70 percent of benzene inhaled may be absorbed through the lungs (ref. 53). In acute poisoning, benzene acts as a narcotic. Chronic poisoning is characterized by damage to the blood-forming tissues and changes in body organs, including the lymph nodes (ref. 54). Inhalation of 210 ppm has resulted in blood disorders for exposed workers (refs. 4,2,9). Benzene can induce chromosomal aberrations in humans (ref. 54).

Benzene is listed in the NIOSH Suspected Carcinogens List. The EPA/NIOSH ordering number is 7222. Inhalation of 2,100 mg/m^3 for 4 years has resulted in cancer in an exposed worker, and large doses of benzene painted repeatedly on the skin of mice have resulted in some incidence of skin carcinomas. TD_{Lo}'s associated with these tests are extremely high and are probably not indicative of the true carcinogenic potential of benzene. An epidemiological study conducted by NIOSH indicates that the incidence of leukemia in workers exposed to benzene is at least five times the expected incidence (ref. 54).

Benzene is toxic to aquatic life: 96 hours. TLm's are reported ranging from 10-100 ppm (ref. 2).

REGULATORY ACTIONS, STANDARDS, CRITERIA, RECOGNITION, CANDIDATE STATUS FOR SPECIFIC REGULATION:

TLV: 30 mg/m^3 (10 ppm). ACGIH classified benzene as an Occupational Substance Suspected of Oncogenic Potential for workers. (Evidence linking benzene to leukemia was limited at the time the TLV was established.)
Benzene appears on EPA Consent Decree List with an assigned priority of 1.
Benzene is the subject of a NIOSH Criteria Document (ref. 55).
The Labor Department has issued emergency temporary standards limiting worker exposure to benzene to 1 ppm as an 8-hour time-weighted average concentration, with a ceiling level of 5 ppm for any 15-minute period during the 8-hour day (ref. 54). The emergency standard is based on conclusive evidence that exposure to benzene presents a leukemia hazard (ref. 54). The standard also prohibits repeated or prolonged skin exposure to liquid benzene.

MINIMUM ACUTE TOXICITY CONCENTRATIONS:

Air, Health: 3.0×10^3 $\mu g/m^3$
Water, Health: $15 \times 3.0 \times 10^3 = 4.5 \times 10^4$ μg/ℓ
Land, Health: $0.002 \times 4.5 \times 10^4 = 90$ μg/g

Air, Ecology:
Water, Ecology: $100 . 10 = 1.0 \times 10^3$ μg/ℓ
Land, Ecology: $0.002 \times 1.0 \times 10^3 = 2$ μg/g

ESTIMATED PERMISSIBLE CONCENTRATIONS:

$EPC_{AH1} = 10^3 \times 30/420 = 71.4$ $\mu g/m^3$
$EPC_{AH1a} = 10/420 = 0.024$ ppm
$EPC_{WH1} = 15 \times 71.4 = 1,071$ μg/ℓ
$EPC_{WH2} = 13.8 \times 30 = 414$ μg/ℓ
$EPC_{LH} = 0.002 \times 414 = 0.83$ μg/g
$EPC_{AC1} = 10^3 \times 3/420 = 7.1$ $\mu g/m^3$
$EPC_{WC} = 15 \times 7.1 = 107$ μg/ℓ
$EPC_{LC} = 0.002 \times 107 = 0.21$ μg/g

$EPC_{WE1} = 50 \times 10 = 500$ μg/ℓ
$EPC_{LE} = 0.002 \times 500 = 1$ μg/g

MULTIMEDIA ENVIRONMENTAL GOALS

X
15
BENZENE

EMISSION LEVEL GOALS							
	I. Based on Best Technology		II. Based on Ambient Factors				
	A. Existing Standards	B. Developing Technology	A. Minimum Acute Toxicity Effluent		B. Ambient Level Goal*		C. Elimination of Discharge
	NSPS, BPT, BAT	Engineering Estimates (R&D Goals)	Based on Health Effects	Based on Ecological Effects	Based on Health Effects	Based on Ecological Effects	Natural Background*
Air, μg/m³ (ppm Vol)			3.0E3		7.1		0.054
Water, μg/l (ppm Wt)			4.5E4	1.0E3	107	500	10†
Land, μg/g (ppm Wt)			9.0E1	2.0E0	0.21	1	

*To be multiplied by dilution factor

AMBIENT LEVEL GOALS					
	I. Current or Proposed Ambient Standards or Criteria		II. Toxicity Based Estimated Permissible Concentration		III. Zero Threshold Pollutants Estimated Permissible Concentration
	A. Based on Health Effects	B. Based on Ecological Effects	A. Based on Health Effects	B. Based on Ecological Effects	Based on Health Effects
Air, μg/m³ (ppm Vol)			71.4 (0.024)		7.1
Water, μg/l (ppm Wt)			414	500	107
Land, μg/g (ppm Wt)			0.83	1	0.21

†Maximum concentration identified in drinking water.

CONTROL TECHNOLOGY ASSESSMENT

- Control System and Disposal Option Information and Design Principles
- Control Process Pollution and Impacts—E. A. Contractors Plus Special Facilities
- Accidental Release, Malfunction, Transient Operation Studies
- Field Testing in Related Applications
- Define Best Control Technology Recommendations

CONTROL TECHNOLOGY ASSESSMENT

Multimedia Environmental Control
Engineering Manual
(Control Approach Categories):

- Gas Treatment
- Liquids Treatment
- Solids Treatment
- Final Disposal
- Process Modification
- Combustion Modification
- Fuel Cleaning
- Fugitive Emissions Control
- Accelerated Release Technology

CONTROL APPROACHES

- **Gas Treatment**
  - Mechanical Collection
  - Electrostatic Precipitators
  - Filters (fabric, granular, etc.)
  - Liquid Scrubbers/Contactors (aqueous, inorganic, organic)
  - Condensers
  - Solid Sorbents (mol sieves, activated carbon)
  - Incineration (direct and catalytic)

- **Liquids Treatment**
  - Settling, Sedimentation
  - Precipitation, Flocculation, Sedimentation
  - Centrifugation and Filtration
  - Evaporation and Concentration
  - Distillation, Flashing
  - Liquid-Liquid Extraction
  - Gas-Liquid Stripping
  - Neutralization
  - Biological Oxidation
  - Wet Thermal Oxidation
  - Activated Carbon Absorption
  - Ion Exchange System
  - Cooling Tower (wet and dry)
  - Chemical Reaction and Separation

- **Solids Treatment**
  - Fixation
  - Recovery/Utilization
  - Processing/Combustion
  - Chemical Reaction and Separation
  - Oxidation/Digestion
  - Physical Separation (specific gravity, magnetic, etc.)

- **Final Disposal**
  - Pond Lining
  - Deep Well Reinjection
  - Burial and Landfill
  - Sealed-Contained Storage
  - Dilution
  - Dispersion

- **Process Modifications**
  - Feedstock Change
  - Stream Recycle

- **Combustion Modification**
  - Flue Gas Recycle
  - Water Injection
  - Staged Combustion
  - Low Excess Air Firing
  - Optimum Burner/Furnace Design
  - Alternate Fuels/Processes

- **Fuel Cleaning**
  - Physical Separation (specific gravity, surface properties, magnetic)
  - Chemical Refining
  - Carbonization/Pyrolysis
  - Liquefaction/Hydrotreating (HDS, HDN, Demetallization)
  - Gasification/Separation

- **Fugitive Emissions Control**
  - Surface Coatings/Covers
  - Vegetation
  - Leak Prevention

- **Accidental Release Technology**
  - Containment Storage
  - Flares
  - Spill Cleanup Techniques

MULTIMEDIA ENVIRONMENTAL CONTROL ENGINEERING MANUAL
(Example of Specific Device Form)

CLASSIFICATION Fuel Cleaning	**GENERIC DEVICE OR PROCESS** Physical Separation - Dense Media Separator of Coal
SPECIFIC DEVICE OR PROCESS Belknap Calcium Chloride Washer[A]	**NUMBER** 7.1.1.3

POLLUTANTS CONTROLLED		**AIR**				**WATER**				**LAND**			
		GASES		**PARTICULATES**		**DISSOLVED**		**SUSPENDED**		**LEACHABLE**		**FUGITIVE DUST**	
	ORGANIC												
X	**INORGANIC**	X	SO_2										
	THERMAL												
	NOISE												

PROCESS DESCRIPTION[B]

Figure 1 shows a schematic diagram of the Belknap calcium chloride washer. Presized and prewetted raw coal enters at the surface of the washer solution and is separated according to the various specific gravities.[C] Refuse settles to the bottom and is removed by a screw conveyor running parallel to the refuse conveyor.[D] Solution within the washer is circulated by two opposing impellers.

The Belknap washer uses calcium chloride solutions ranging in specific gravity from 1.14 to 1.25. These solutions are circulated through the washer in an upward direction to produce an effective specific gravity of 1.40 to 1.60. Both flow and density are carefully controlled to provide the desired separation.

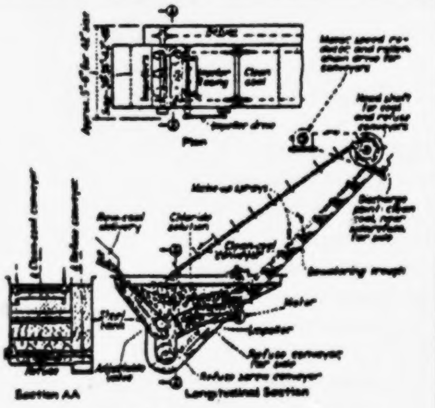


Figure 1. THE BELKNAP CALCIUM CHLORIDE WASHER (1)

A second method which could be used to control the specific gravity within the washer is to wash the coal product with a calcium chloride solution to remove any suspended solids (slimes). This dense solution is then recycled to the washer to maintain the right specific gravity. In this case, the calcium chloride is used more as a stabilizing agent than the dense media itself. If the suspended solids from the washed coal product can be recycled back to the washer, the amount of calcium chloride required for density control can be reduced. In this way, the solids which naturally occur in the coal can be used to maintain the heavy density medium. Considerations of this type could improve the economics of this systems over other dense medium systems which utilize material from an outside source for density control, e. g. Magnetite Processes.

The washed coal product leaving the system has a considerable amount of entrained calcium chloride solution. This entrainment can reduce potential problems in coal dusting and freezing. The loss of calcium chloride, however, may limit the economic application of the process to coarser sizes of coal.

APPLICATION RANGE

OPERATING RANGES	METRIC (SI)		ENGLISH	
TEMPERATURE	20	°C	68	°F
PRESSURE	101.3	KPa	14.7	psi
VOLUMETRIC RATE	--	m³/s	--	ft³/min
MASS RATE	--	kg/s	--	lb/hr
ENERGY RATE	--	J/s	--	BTU/hr

The effective specific gravity within the washer can be adjusted from 1.40 to 1.60 by varying the solution density or recirculation rate. Consequently, the range of physical separation is limited to a specific gravity within this range.

Feed sizes can range from 8-in. (20.3 cm) to 3/8 in. (.95 cm), however, the feed to a single unit should not fluctuate very much. The size range that can be washed in a standard washer can be varied up to a 4:1 ratio, but should be limited to 3:1 or 2:1 if possible.

CAPITAL COSTS

OPERATING COST

OPERATING EFFICIENCIES

The recovery efficiency for coal coarser than 1/4-inch is 95 to 99% of the laboratory float sink tests. Trace elements association and removal characteristics for the physical separation of coal in general are shown in Table 1. The level of fluorine, which is present as part of the mineral apatite, would also be reduced. The chlorine and bromine contaminants (as well as the sodium and potassium associated with them) which are commonly present as the mineral halite would be removed along with other matter removed during coal benefication, (3).

Table 1. TRACE ELEMENT ASSOCIATION AND REMOVAL CHARACTERISTICS

Association	Trace Elements	Expected Removal
Organic	Ge, Be, B and U	None
More organic	P, Ga, Ti, V, and Sb	Small Amount
More mineral	Co, Ni, Cr, Se and Cu	Partial
Mineral	Hg, Zn, Cr, Cd, As, Pb, Mo, and Mn	Signficant

NOTES

A) For other dense media separators, see all devices under 7.1.1 and 7.1.2.

B) Based on information from the Process Machinery Division of the Arthur G. McKee & Co., (reference 1)

C) This device can also be used in a secondary circuit to separate sink product from a primary separator into middlings and refuse.

D) Units can be designed with the separating compartment divided into two parallel sections. Each section would be equipped with individual medium circulation systems thus making it possible to wash a much wider range in one machine.

ENVIRONMENTAL PROBLEMS

Coal preparation reduces stack gas emissions but may also create pollution problems in the following areas.

1) land pollution created by refuse disposal.

2) water pollution from the leaching of oxidized refuse material.

3) air pollution from the spontaneous combustion of refuse piles.

MANUFACTURER / SUPPLIER

ASV Engineering Ltd.
GEOMIN
Minerals Processing Co., Div. of Trojan Steel Co.
Process Machinery Division, Arthur G. McKee & Company

REFERENCES

1) Mitchell, David R., and Leonard, Joseph W., ed. Coal Preparation, AIME, New York, Second Edition, (1950); Third Edition, (1968).

2) Lowry, H. H., ed., Chemistry of Coal Utilization, John Wiley and Sons, New York, First Edition, (1945); Second Edition (1963).

3) Mezey, E. J., Singh, S., and Hissong, D. W., "Fuel Contaminants: Volume I, Chemistry " EPA 600/2-76-177a, (1976).

CONTROL TECHNOLOGY ASSESSMENT

Multimedia Environmental Control Engineering Manual (Stepwise guidance for defining specific control options for specific situations):

- Medium Phase (gas, liquid, solid)
- Medium Description (combustible gases, black water, coal cleaning waste, etc.)
- Medium Physical Properties (temperature, pressure)
- Pollutant Species Present
- Pollutant Concentration
- General Technology (physical, chemical treatment; prevention of pollutant formation; final disposal)
- Generic Device (ESP, dry inertial collector, etc.)
- Specific Device (commercial devices and specifications)

STANDARDS OF PRACTICE MANUALS

- Subject
  - A uniquely different basic energy process (at the commercial demonstration stage) in a particular industry
- Example
  - Low-Btu Gasification - Wellman Galusha
- Aim
  - Provide an integrated, multimedia, industry-oriented, single-package review of the environmental requirements, guidelines and best control/disposal options. Accounts for variations needed for different regional site alternatives.

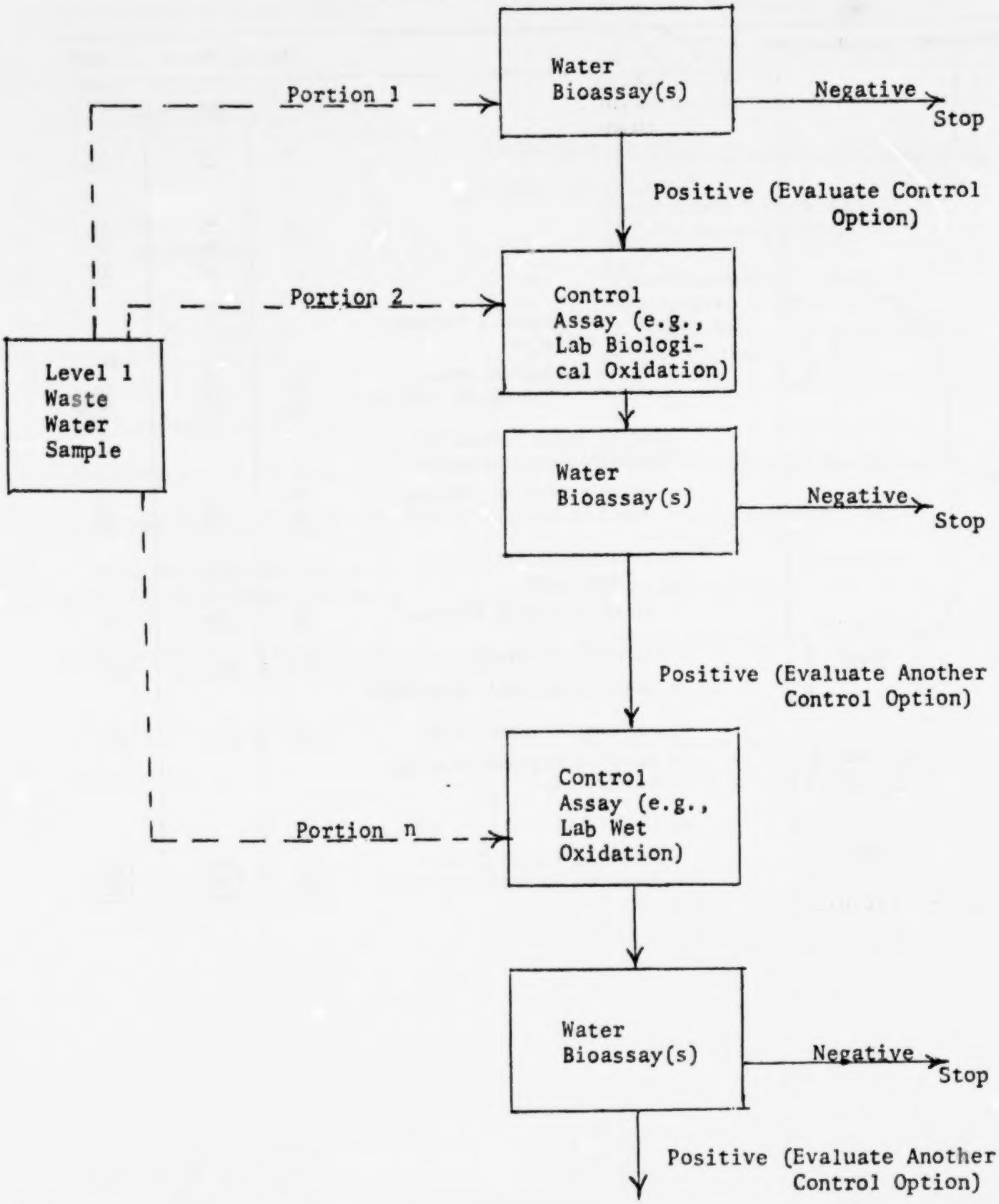
CONTROL TECHNOLOGY ASSESSMENT

Standards of Practice Manual Outline

- Summary
- Outline of Basic Process
  - Process Modules
  - Control/Disposal Modules
  - Control/Disposal Costs
  - Variations Resulting from Regional Siting Factors
- Existing Environmental Requirements
  - Existing Standards
    - Air
    - Water
    - Land
  - Other Environmental Requirements
  - Environmental Guidelines
  - Regional Considerations
- Environmental Emissions and Factors Achievable
  - Criteria
  - MEG (Pollutant)
  - MEG (Nonpollutant)
- Best Control/Disposal Practice
  - Gas Treatment
  - Liquids Treatment
  - Solids Treatment
  - Final Disposal
  - Combustion Modification
  - Fuel Cleaning
  - Fugitive Emissions Control
  - Accidental Release Technology
  - Regional Variations
- Detailed Definition of Basic Process
  - Process Module No. 1
    - Source Unit Operations (Unit Operations Pollutant Sources)
      - Control Options/Emissions/Costs
        - Commercially Operated
        - Commercially Operated on a Different Process/Industry
        - Pilot Data Available
  - Process Module No. 2, 3 ...
  - Process Module No. n

CONTROL TECHNOLOGY ASSESSMENT

Control Assay Example


Level 1 Waste Water Sample
Portion 1
Water Bioassay(s)
Negative
Stop
Positive (Evaluate Control Option)
Portion 2
Control Assay (e.g., Lab Biological Oxidation)
Water Bioassay(s)
Negative
Stop
Positive (Evaluate Another Control Option)
Portion n
Control Assay (e.g., Lab Wet Oxidation)
Water Bioassay(s)
Negative
Stop
Positive (Evaluate Another Control Option)

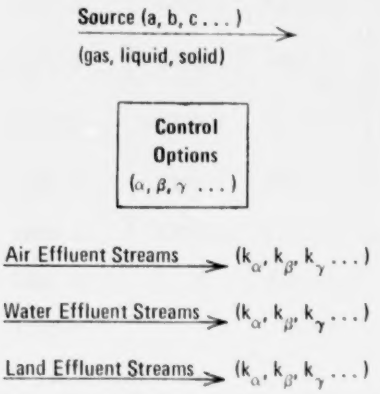
ASSESSMENT ALTERNATIVES USING MEG'S

ASSESSMENT ALTERNATIVES			Air	Water	Land
			MEG Types		
	BT	° Existing standards	1A	1W	1L
	BT	° Developing technology			
		- 1983	2A	2W	2L
		- 1988	3A	3W	3L
		- 1993	4A	4W	4L
EPC	ES	° Current vs Proposed Ambient Stds or Criteria			
		- Based on Health Effects	5A	5W	5L
		- Based on Ecological Effects	6A	6W	6L
		° Toxicity Based Estimated Permissible Concentration			
		- Based on Health Effects	7A	7W	7L
		- Based on Ecological Effects	8A	8W	8L
		° Zero Threshold Pollutants Est. Perm. Conc.			
		- Based on Health Effects	9A	9W	9L
	NB	° Elimination of Discharge	10A	10W	10L
		- Based on Natural Background			
	SD	° Significant Deterioration	11A	11W	11L
		- Based on Regional Average Backgrounds			
	MATE	° Minimum Acute Toxicity Effluent			
		- Based on Health Effects	12A	12W	12L
		- Based on Ecological Effects	13A	13W	13L

ENVIRONMENTAL ALTERNATIVES ANALYSES

Source Analysis Models (SAM's)

- SAM/IA - For Rapid Screening
- SAM/I - For Screening
- SAM/II - General Approach to Evaluating any U.S. Regional Site Alternative



Source (a, b, c . . .) $\rightarrow$

(gas, liquid, solid)

Control Options
$(\alpha, \beta, \gamma \ldots)$

Air Effluent Streams $\rightarrow (k_\alpha, k_\beta, k_\gamma \ldots)$

Water Effluent Streams $\rightarrow (k_\alpha, k_\beta, k_\gamma \ldots)$

Land Effluent Streams $\rightarrow (k_\alpha, k_\beta, k_\gamma \ldots)$

SCHEMATIC IDENTIFICATION OF SOURCES/CONTROL-OPTIONS/EFFLUENTS

ENVIRONMENTAL ALTERNATIVES ANALYSES

Assessment Alternatives

- Best Technology (BT)
- Minimum Acute Toxicity Effluent (MATE)
- Existing Ambient Standards (ES)
- Estimated Permissible Concentration (EPC)
- Natural Background/Elimination of Discharge (NB)
- Significant Deterioration (SD)

ENVIRONMENTAL ALTERNATIVES ANALYSIS

Source Analysis Model SAM/IA
(For Rapid Screening)

- Effluent Concentration Basis
- Assessment Alternative: (MATE)
- No Transport/Transformation Analysis
- Degree of Hazard Calculation
- Toxic Unit Discharge Rate Calculation

ENVIRONMENTAL ALTERNATIVES ANALYSIS

Source Analysis Model
Basic Calculations

- For a specific MEG pollutant:

$$\underline{\text{H = degree of hazard}}\ \text{(severity)} = \frac{\text{C pollutant}}{C_{\text{MEG}}}$$

- For a complex effluent:

$$\underline{\text{Toxic Unit Discharge Rate}} = \text{(mass or volumetric discharge rate)} \times \sum H$$

Category	Compound	Air µg/m^3 (ppm)		Water µg/ℓ		Land µg/ℓ
		Health	Ecology	Health	Ecology	
14B	Dimethyl sulfoxide	8.14E2		1.22E3	N	2.44E0
15	Benzene	3.00E3 (1)		4.50E4	1.00E3	2.00E0
	Toluene	3.75E5 (100)		5.63E6	1.00E3	2.00E0
	Ethylbenzene	4.35E5 (100)		6.53E6	1.00E3	2.00E0
	Styrene	4.20E5 (100)		6.30E6	1.00E3	2.00E0
	Propylbenzene	2.17E5		3.25E6	1.00E3	2.00E0
	Isopropylbenzene	6.30E4		9.45E5	1.00E3	2.00E0
	Butylbenzene	2.25E5		3.38E6	N	6.76E3
	Biphenyl	1.00E3		1.5E4	N	3.00E1
	4,4'-Diphenylbiphenyl	N		N	N	N
	Xylenes	4.35E5 (100)		6.53E6	1.00E3	2.00E0
	Dialkylbenzenes	2.25E5		3.38E6	1.00E3	2.00E0
	Tetrahydronaphthalenes	1.29E5		1.94E6	1.00E3	2.00E0
	Dihydronaphthalenes	1.27E5		1.91E6	N	3.82E3
	Terphenyls	9.00E3 (1)			N	2.70E2
	Trimethylbenzenes					
	Tetramethylbenzenes					
16A	Chlorobenzene					
	Bromo and Dibromobenzenes					
	Bromochlorobenzenes					

-----------Example Page-----------

(DRAFT--5/10/77)

MINIMUM ACUTE TOXICITY EFFLUENT (MATE)
VALUES FOR ORGANIC AND INORGANIC
COMPOUNDS FROM FOSSIL ENERGY PROCESSES

A Subset of Multimedia Environmental Goals
for Environmental Assessment Use in
Rapid Screening of Effluents

SAM/IA SUMMARY SHEET

Form IA01

1. SOURCE AND APPLICABLE CONTROL OPTIONS

2. PROCESS THROUGHPUT OR CAPACITY

3. USE THIS SPACE TO SKETCH A BLOCK DIAGRAM OF THE SOURCE AND CONTROL ITEMS SHOWING ALL EFFLUENT STREAMS. INDICATE EACH STREAM WITH A CIRCLED NUMBER USING 101-199 FOR GASEOUS STREAMS, 201-299 FOR LIQUID STREAMS AND 301-399 FOR SOLID WASTE STREAMS.

4. LIST AND DESCRIBE GASEOUS EFFLUENT STREAMS USING RELEVANT NUMBERS FROM STEP 3.

101 ____________________

102 ____________________

103 ____________________

5. LIST AND DESCRIBE LIQUID EFFLUENT STREAMS USING RELEVANT NUMBERS FROM STEP 3.

201 ____________________

202 ____________________

203 ____________________

6. LIST AND DESCRIBE SOLID EFFLUENT STREAMS USING RELEVANT NUMBERS FROM STEP 3.

301 ____________________

302 ____________________

303 ____________________

7. FOR EACH EFFLUENT STREAM COMPLETE FORM IA02.

8. LIST SUMS FROM LINE 7, FORMS IA02, IN TABLE BELOW

TOXIC DISCHARGE UNITS BY EFFLUENT STREAM								
GASEOUS (m³/SEC)			LIQUID (l/SEC)			SOLID (g/SEC)		
STREAM CODE	TOXIC DISCHARGE UNITS		STREAM CODE	TOXIC DISCHARGE UNITS		STREAM CODE	TOXIC DISCHARGE UNITS	
	HEALTH BASED	ECOL. BASED		HEALTH BASED	ECOL. BASED		HEALTH BASED	ECOL. BASED
A	B	C	D	E	F	G	H	I

9. SUM SEPARATELY GASEOUS, LIQUID AND SOLID TOXIC DISCHARGE UNITS FROM TABLE IN LINE 8 (I.E., SUM COLUMNS):

TOTAL TOXIC DISCHARGE UNITS

	HEALTH BASED	ECOLOGICAL BASED
GASEOUS	(Σ Col. B) 9a ______	(Σ Col. C) 9a' ______
LIQUID	(Σ Col. E) 9b ______	(Σ Col. F) 9b' ______
SOLID	(Σ Col. H) 9c ______	(Σ Col. I) 9c' ______

10. NUMBER OF EFFLUENT STREAMS

GASEOUS 10a ______
LIQUID 10b ______
SOLID 10c ______

11. AVERAGE TOXIC DISCHARGE UNIT RATES

	HEALTH BASED	ECOLOGICAL BASED
GASEOUS	(9a/10a) 11a ______	(9a'/10a) 11a' ______
LIQUID	(9b/10b) 11b ______	(9b'/10b) 11b' ______
SOLID	(9c/10c) 11c ______	(9c'/10c) 11c' ______

12. LIST POLLUTANT SPECIES KNOWN OR SUSPECTED TO BE EMITTED FOR WHICH NO MATES ARE AVAILABLE.

1. SOURCE/CONTROL OPTION

2. EFFLUENT STREAM

CODE # ________ NAME ________________________________

3. EFFLUENT STREAM FLOW RATE

Q = ____________

(air = m³/sec — liquid = l/sec — solid = g/sec)

4. COMPLETE THE FOLLOWING TABLE FOR THE EFFLUENT STREAM OF LINE 2 (USE BACK OF FORM FOR SCRATCH WORK)

A	B	C	D	E	F	G	H	I	J	K	L
POLLUTANT SPECIES	EMISSION FACTOR	POLLUTANT FLOW RATE (B X CAPACITY)	POLLUTANT CONCENTRATION (C/LINE 3)	HEALTH MATE CONCENTRATION	ECOLOGICAL MATE CONCENTRATION	DEGREE OF HEALTH HAZARD (D/E)	DEGREE OF ECOLOGICAL HAZARD (D/F)	CHECK (√) IF HEALTH MATE EXCEEDED	CHECK (√) IF ECOLOGICAL MATE EXCEEDED	TOXIC UNIT FLOW RATE (HEALTH BASED) (G X LINE 3)	TOXIC UNIT FLOW RATE (ECOLOGICAL BASED) (H X LINE 3)
UNITS						—	—	—	—		

5. EFFLUENT STREAM TOXIC UNIT CONTENT

HEALTH MATE BASED (Σ COL. G) 5a ______

ECOLOGICAL MATE BASED (Σ COL. H) 5b ______

6. NUMBER OF POLLUTANTS COMPARED TO MATES

N = ______

7. TOXIC UNIT DISCHARGE RATE

HEALTH BASED (LINE 3 X LINE 5a + N) 7a ______

ECOLOGICAL BASED (LINE 3 X LINE 5b + N) 7b ______

ENVIRONMENTAL ALTERNATIVES ANALYSIS

Outlines for the More Detailed Proposed Source Analysis Models

- *Source Analysis Model (SAM/I) - (For Screening)*
  - Effluent Concentration Basis
  - Assessment Alternatives: Bt, Es, EPC, NB, and SD
  - Effluent Transport/Transformation Analysis (ETTA) - (very approximate)
  - Remaining Steps, Starting with Degree-of-Hazard Calculation or other Ratios, are Similar to SAM/IA

- *Source Analysis Model (SAM/II) -(General Approach to Evaluating any U.S. Regional Site Alternative)*
  - Ambient Concentration Basis
  - Assessment Alternatives: BT, ES, EPC, NB, and SD
  - Recommended Transport/Transformation Models
  - Remaining Steps, Starting with Degree-of-Hazard or Other Calculations, Are Similar to SAM/IA
  - Application of Other Factors or Decision Criteria

PRELIMINARY EXAMPLES OF CONTROL/ CONTROL DEVELOPMENT NEEDS FOR SYNTHETIC FUELS (EXCLUDING PHYSICAL COAL CLEANING PRETREATMENT)

- Gas Treatment
  - Particulate control from coal conveying, load and discharge hoppers, gas purges on transport, coal thermal pretreatment, and coal burning for power
  - Particulate control in converter via baffles, velocity gradients
  - Particulate control in raw gas via water scrubbing cyclones
  - Tar and oil removal from raw gas via liquid scrubbing
  - Tar and oil removal from raw gas via cooling
  - Gaseous contaminants (H_2S, COS, NH_3, trace metals) removal from raw gas via liquid scrubbing
  - Sulfur compound removal from pre-final product gas via guard chamber (physical or chemical)
  - Contaminant removal from vents via scrubbing or combustion
  - Product "polishing" via activated carbon
  - Use or disposal of volatiles from pretreatment

- Liquid Treatment
  - Treatment of run off from storage and process areas via holding ponds
  - Boiler and cooling tower blowdown water treatment
  - Heat exchange for liquid temperature control
  - Treatment of water from tar/oil liquid separators
  - Treatment of water from scrubbers
  - Stripping of constituents from liquids
  - Filtration of liquid products/by-products
  - Contaminant removal from products and by-products
  - By-product separation from water (e.g., phenolsolvan)
  - Effluent pH control
  - Effluent biological treatment
  - Effluent carbon "polishing"

- Solids Treatment
  - Sulfur from Claus or Stretford
  - Char recovery and beneficiation
  - Sludge treatment for valuable constituents
  - Treatment of sludge from biox for fixation or neutralization
  - Sludge fixation from holding ponds
  - Used filter precoat and filtered material recovery and treatment for heating value or constituent recovery
  - Catalyst recovery of deposited materials and/or disposal
- Final Disposal
  - Containment of solid waste disposal area leachate contaminants

- Control of airborne contaminants from solid waste area (e.g., odors)
- Land reuse guidelines
- Site maintenance/surveillance

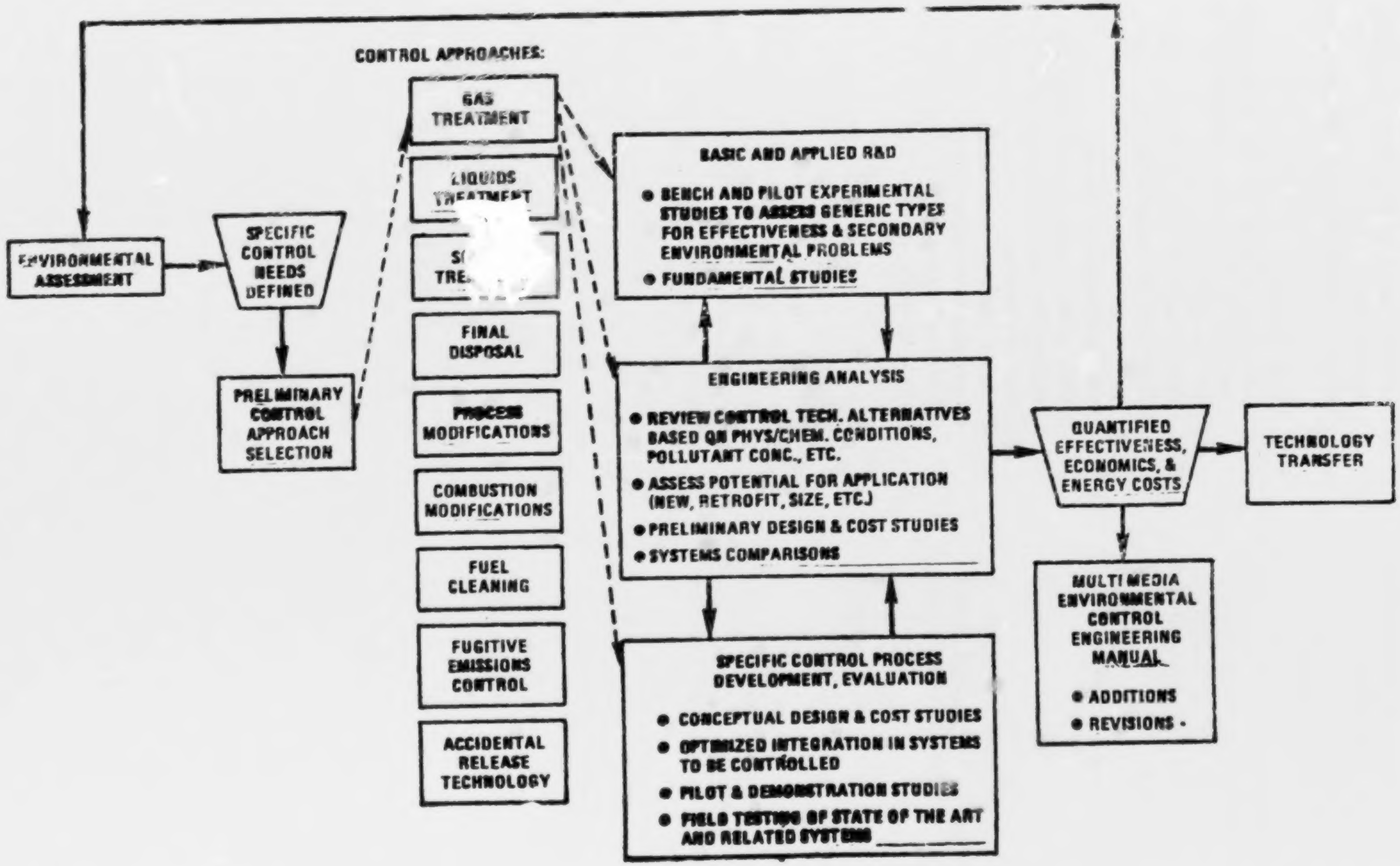
- Process Modifications
  - Selective pretreatment of coal for control of input to the converter via physical, chemical, or pretreatment condition changes
  - Converter operating condition changes for pollutant chemical or physical form change
  - Utilization of alternate technologies for conversion or treatment
  - Improved COS removal technique
  - Improve mechanism for coal feed to converter for reduction of pollutant release
  - Closed circuit liquid cooling
  - Minimization of coal drying and use of water in converter for hydrogen

- Combustion Modifications
  - NO_x, SO_x, and other pollutant control for char combustion
  - NO_x control for high nitrogen liquid fuel products
  - Control for low-Btu, COS containing waste gases
  - Flare improvement for upset conditions

- Fuel Cleaning
  - Selective removal of pollutant constituents or pollutant forming catalysts in pretreatment
  - Beneficiation of char for combustion
  - HDS/HDN for liquid fuels

- Fugitive Emissions Control
  - Coal piles, product and by-product storage for solids via protective coverings or coatings
  - Liquid storage or holding areas via chemical or physical means
  - Improved maintenance and/or equipment for seals, transfer points

- Accidental Release Technology
  - Contingency containment of liquids
  - Burst discs leading to control mechanisms or expansion chambers
  - Emergency cleanup procedures
  - Evaluation of special cold climate effects on failure probabilities (e.g., freezing of drains)


ENVIRONMENTAL ASSESSMENT
SPECIFIC CONTROL NEEDS DEFINED
PRELIMINARY CONTROL APPROACH SELECTION
CONTROL APPROACHES:
GAS TREATMENT
LIQUIDS TREATMENT
S TRE
FINAL DISPOSAL
PROCESS MODIFICATIONS
COMBUSTION MODIFICATIONS
FUEL CLEANING
FUGITIVE EMISSIONS CONTROL
ACCIDENTAL RELEASE TECHNOLOGY
BASIC AND APPLIED R&D
● BENCH AND PILOT EXPERIMENTAL STUDIES TO ASSESS GENERIC TYPES FOR EFFECTIVENESS & SECONDARY ENVIRONMENTAL PROBLEMS
● FUNDAMENTAL STUDIES
ENGINEERING ANALYSIS
● REVIEW CONTROL TECH. ALTERNATIVES BASED ON PHYS/CHEM. CONDITIONS, POLLUTANT CONC., ETC.
● ASSESS POTENTIAL FOR APPLICATION (NEW, RETROFIT, SIZE, ETC.)
● PRELIMINARY DESIGN & COST STUDIES
● SYSTEMS COMPARISONS
SPECIFIC CONTROL PROCESS DEVELOPMENT, EVALUATION
● CONCEPTUAL DESIGN & COST STUDIES
● OPTIMIZED INTEGRATION IN SYSTEMS TO BE CONTROLLED
● PILOT & DEMONSTRATION STUDIES
● FIELD TESTING OF STATE OF THE ART AND RELATED SYSTEMS
QUANTIFIED EFFECTIVENESS, ECONOMICS, & ENERGY COSTS
TECHNOLOGY TRANSFER
MULTIMEDIA ENVIRONMENTAL CONTROL ENGINEERING MANUAL
● ADDITIONS
● REVISIONS

RELATIONSHIP OF CONTROL TECHNOLOGY DEVELOPMENT TO ENVIRONMENTAL ASSESSMENT DIAGRAM

APPENDIX A

ENVIRONMENTAL ASSESSMENT STEERING COMMITTEE

Robert P. Botts
Ecosystems Modeling & Analysis Br.
Environmental Research Laboratory
Environmental Protection Agency
200 SW 35th Street
Corvallis, Oregon 97330
FTS: 8-420-4679

Dale A. Denny
Industrial Processes Division, MD-62
Industrial Environmental Research Laboratory
Environmental Protection Agency
Research Triangle Park, N.C. 27711
FTS: 8-629-2547

James A. Dorsey
Industrial Processes Division, MD-62
Industrial Environmental Research Laboratory
Environmental Protection Agency
Research Triangle Park, N.C. 27711
FTS: 8-629-2557

Robert P. Hangebrauck
Director, Energy Assessment & Control
Division, MD-61
Industrial Environmental Research Laboratory
Environmental Protection Agency
Research Triangle Park, N.C. 27711
FTS: 8-629-2825
919/541-2825

Clyde J. Dial
Director, Program Operations Office
Industrial Environmental Research Laboratory
Environmental Protection Agency
5555 Ridge Avenue
Cincinnati, Ohio 45268
FTS: 8-684-4438

Stan Hegre
Environmental Research Laboratory
Environmental Protection Agency
South Ferry Road
Narragansett, R. I. 02882
FTS: 8-834-4843, ext. 240

Bill Horning
Newtown Fish Toxicology Station
3411 Church Street
Cincinnati, Ohio 45244
FTS: 8-684-8601

Joellen Huisingh
Health Effects Research Laboratory, MD-82
Environmental Protection Agency
Research Triangle Park, N.C. 27711
FTS: 8-629-2537

Norbert Jaworski
Deputy Director, Industrial Environmental
Research Laboratory, MD-60
Environmental Protection Agency
Research Triangle Park, N.C. 27711
FTS: 8-629-2821

Larry D. Johnson
Industrial Processes Division, MD-62
Industrial Environmental Research Laboratory
Environmental Protection Agency
Research Triangle Park, N.C. 27711
FTS: 8-629-2557

Julian W. Jones
Utilities & Industrial Power Division, MD-61
Industrial Environmental Research Laboratory
Environmental Protection Agency
Research Triangle Park, N.C. 27711
FTS: 8-629-2489

Walt Sanders
Environmental Research Laboratory
Environmental Protection Agency
College Station Road
Athens, Ga. 30601

Jerry Stara
Health Effects Research Laboratory
Environmental Protection Agency
Cincinnati, Ohio 45268
FTS: 8-684-7406
Commercial: 513/684-7407

Martin Stepanian
Industrial Environmental Research Laboratory
Environmental Protection Agency
5555 Ridge Avenue
Cincinnati, Ohio 45268
FTS: 8-684-4439

W. Gene Tucker
Special Studies Staff, MD-63
Industrial Environmental Research Laboratory
Environmental Protection Agency
Research Triangle Park, N.C. 27711
FTS: 8-629-2745

Jerry Walsh
Environmental Research Laboratory
Environmental Protection Agency
Sabine Island
Gulf Breeze, Florida 32561
FTS Operator: 8-946-2011
Commercial: 904/932-5311

Mike D. Waters
Health Effects Research Laboratory, MD-82
Environmental Protection Agency
Research Triangle Park, N.C. 27711
FTS: 8-629-2537

DEVELOPMENT OF MULTIMEDIA ENVIRONMENTAL GOALS (MEG's) FOR POLLUTANTS FROM FUEL CONVERSION PROCESSES

By
Garrie L. Kingsbury
Research Triangle Institute
Research Triangle Park, N. C.

Abstract

The presentation will highlight the progress to date in developing a systematic approach to describe multimedia environmental goals for chemical substances associated with fuel conversion processes. Discussion will focus on (1) the various types of information pertinent to environmental goals and available for a multiplicity of potential chemical contaminants and (2) models designed to incorporate available data in the prediction of permissible ambient or emission concentrations for each substance. The validity of combining various models in order to assign priorities or to compare distinctly different toxicants based on their respective environmental goals will be addressed. Comments on future work directed toward refinement and expansion of the methodology will also be included.

INTRODUCTION

Multimedia Environmental Goals (MEG's) are levels of contaminants or degradants (in ambient air, water, or land or in emissions or effluents conveyed to ambient media) that are judged to be (1) appropriate for preventing certain negative effects in the surrounding populations or ecosystems, or (2) representative of the control limits achievable through technology.

Establishing Multimedia Environmental Goals is an integral part of the environmental assessment methodology that is currently being developed under the guidance of the Fuels Process Branch of IERL/EPA at RTP. Environmental assessment involves:

1) The determination of contaminant levels associated with emissions and effluents from a point source.
2. Comparison of those determinations with desirable control levels.

The need for MEG's arises in this latter aspect of environmental assessment.

The MEG's project has been conceived to supply sets of control goals for specific chemical contaminants, complex effluents, and non-chemical degradents based on some of the criteria options that might be considered in defining "desirable control levels." These sets of goals, then, provide the values to be compared with actual contamination levels for environmental assessment purposes.

The first year of MEG's development was devoted largely to selecting the options to be used as MEG's criteria and to investigating ways to approach the problem of defining MEG's for a large number of chemical substances. Initially, the objective of this work was to describe MEG's for chemical pollutants associated with coal conversion processes. However, the value of an expanded list of contaminants was recognized, and the potential for extended application of a MEG's methodology called for the development of a broad, systematic, and adaptable approach for addressing a much larger number of chemical and non-chemical pollutants. Hence the scope of the MEG'sproject has been expanded to encompass a broad range of objectives which include the following:

1) Compiling a Master List of all chemical contaminants, complex effluents/mixtures, and non-chemical degradants (such as visual effects, subsidence, heat, and noise) to be addressed by MEG's. (The list is to include but should not be limited exclusively to contaminants from fossil fuels processes.)
2) Arrangement of the chemical substances appearing on the Master List into a practical catalog to provide a useful tool for environmental assessment.
3) Design of a format conducive to the concurrent presentation of sets of Emission Level Goals and Ambient Level Goals. (The format should allow ready comparison of the MEG's within a set as well as facilitating comparison of different substances.)

4) Determination of the kinds of data pertinent to desirable control levels and the availability of that data. A format for presenting background information should be established to accompany MEG's specified for each chemical substance.
5) Development of a methodology to establish meaningful values to serve as MEG's for each chemical substance on the Master List. (The methodology should incorporate as MEG's those Federal standards, criteria, and recommendations pertinent to chemical substances.)
6) Presentation, according to the format prescribed, of a set of Emission Level Goals and Ambient Level Goals for each chemical substance appearing on the Master List. (These MEG's should be accompanied by qualitative supporting data.)

The central purpose of the project remains the derivation of Multimedia Environmental Goals as estimates of desirable levels of control for those chemical contaminants and nonchemical degradents included in a master list.

COMPILATION OF THE MASTER LIST OF CHEMICAL SUBSTANCES AND PHYSICAL AGENTS

A Master List of more than 600 chemical substances and physical agents has been compiled using selection factors prescribed by EPA. Primary emphasis has been placed on contaminants from fossil fuels processes (particularly coal gasification and liquefaction), and the Master List has been compiled largely on the basis of the literature pertinent to these processes. Process streams were characterized both qualitatively and quantitatively wherever possible to provide insight for selecting substances likely to be present but not mentioned specifically in the process literature.

Three levels of priority were assigned to the selection factors to determine what substances (of all possible chemical substances and physical agents that might be described as environmental contaminants) would be entered on the Master List for MEG's. The selection factors are outlined below:

Primary Selection Factors

1) The pollutant is associated with fossil fuels processes.

All those individual substances or classes of substances known or suspected to be present in the emissions or effluents from fossil fuels processes must appear on the Master List.

Secondary Selection Factors

1) Federal standards or criteria exist or have been proposed (ambient, emission, or occupational).
2) A TLV has been established or an LD_{50} has been reported.
3) The substance has been listed as a suspected carcinogen.
4) The substance appears on the EPA Consent Decree list.

Compounds that meet any one of the four secondary selection factors and are representative of a class of compounds associated with fossil fuels processes must appear on the Master List.

Tertiary Selection Factors
(Optional)

1) The substance is present as a pollutant in the environment.
2) The substance has been identified as being highly toxic.

Consideration for inclusion in the Master List is also to be given to certain additional pollutants, not necessarily associated with fossil fuels processes, provided they satisfy either of the tertiary selection factors.

ORGANIZATION OF THE MASTER LIST

To organize the more than 600 Master List entries, a system for ordering the substances had to be developed. The approach ultimately determined to meet the need for organization most effectively involves clustering substances into categories based on chemical functional groups for organic compounds and on principle element for inorganics. The categories are then arranged to provide a coordinated framework for the list. This categorization scheme, besides organizing the list of chemical contaminants into manageable chunks, emphasizes logical relationships between groups of substances so that each category is characterized by toxicologically and chemically similar substances.

A total of 85 categories (26 organic and 59 inorganic) are required to logically organize specific chemical contaminants included in the Master List for MEG's.

Generalizations and extrapolations are often valid among the compounds included within a category, allowing data gaps to be filled in some instances. Substances likely to occur together or to behave similarly in an organism may become apparent through the categorization scheme. Also, methods of detection for compounds within a specific category are likely to be similar, and analysis of a category as a whole may in some cases be practical for broad screening applications.

The categorization scheme allows one seeking information on a particular substance to find material of value associated with a related compound or element, should the particular item of interest be missing from the compilations. The utility of isolating related compounds by categorization has become very evident during the course of data collection for the current MEG's work. For example, phenolic compounds are addressed collectively by water quality recommendations;[1] since phenols are grouped as a category in the compilations, it is easy to comprehend the intended subject of the recommendation.

An alphabetical arrangement of Master List entries, although in some ways the simplest approach to organizing the list, has been avoided since it would provide no means of associating related compounds (unless of course their names begin with the same letter).

THE MULTIMEDIA ENVIRONMENTAL GOALS CHART

A MEG's chart has been designed to display concurrently Emission Level Goals and Ambient Level Goals for any specific chemical contaminant in a consistent, easy to use format. The current version of the chart is shown in Figure 1.

The MEG's chart consists of two interrelated tables, one addressing Emission Level Goals and one addressing Ambient Level Goals. Each table is divided into columns devoted to specific criteria for describing desirable control levels (for example, Toxicity Based Ambient Level Goals [Based on Health Effects]). Within each column, space is provided for concentration levels to be specified for air, water, and land in units consistent with those indicated in the index column at the left. Only numbers will appear within the MEG's charts. The name of the substance addressed, its category number, and appropriate toxicity indicator (based on human health effects associated with the substance as an air contaminant) are all presented in bold letters in the upper right hand corner of each chart.

Emission Level Goals

Emission Level Goals presented in the top half of the MEG's chart actually pertain to gaseous emissions to the air, aqueous effluents to water, and solid waste to be disposed to land. These Goals may have as their bases technological factors or ambient factors. Technological factors refer to the limitations placed on control levels by technology, either existing or developing (i.e., equipment capabilities or process parameters). The Standards of Performance for New Stationary Sources[2] provide an example of promulgated Emission Level Goals based on technology.

Since there is obviously a relationship between contaminant concentrations in emissions and the presence of these contaminants in ambient media, it is imperative to consider ambient factors when establishing emission level goals. Ambient factors included in the MEG's chart as criteria for Emission Level Goals include:

1) Minimum Acute Toxicity Effluents (MATE's)—concentrations of pollutants in undiluted emission streams that would not adversely affect those persons or ecological systems exposed for short periods of time.
2) Ambient Level Goals—i.e. estimated permissible concentrations (EPC's) of pollutants in emission streams which, after dispersion, will not cause the level

MULTIMEDIA ENVIRONMENTAL GOALS

EMISSION LEVEL GOALS							
	I. Based on Best Technology		II. Based on Ambient Factors				
Category	A. Existing Standards	B. Developing Technology	A. Minimum Acute Toxicity Effluent		B. Ambient Level Goal*		C. Elimination of Discharge
	NSPS, BPT, BAT	Engineering Estimates (R&D Goals)	Based on Health Effects	Based on Ecological Effects	Based on Health Effects	Based on Ecological Effects	Natural Background*
Air, μg/m^3 (ppm Vol)							
Water, μg/l (ppm Wt)							
Land, μg/g (ppm Wt)							

*To be multiplied by dilution factor

	AMBIENT LEVEL GOALS				
	I. Current or Proposed Ambient Standards or Criteria		II. Toxicity Based Estimated Permissible Concentration		III. Zero Threshold Pollutants Estimated Permissible Concentration
	A. Based on Health Effects	B. Based on Ecological Effects	A. Based on Health Effects	B. Based on Ecological Effects	Based on Health Effects
Air, μg/m^3 (ppm Vol)					
Water, μg/l (ppm Wt)					
Land, μg/g (ppm Wt)					

Figure 1. Current version of multimedia environmental goals chart.

of contamination in the ambient receiving medium to exceed a safe continuous exposure concentration.

3) Elimination of Discharge (EOD) — concentrations of pollutants in emission streams which, after dilution, will not cause the level of contamination to exceed levels measured as "natural background."

Although technology based Emission Level Goals are highly source specific, goals based on ambient factors can be considered universally applicable to discharge streams for any industry. The Emission Level Goals based on EPC's for example, correspond to the most stringent Ambient Level Goals (dilution factor to be applied) appearing in the MEG's chart, regardless of source of emission. This format for presentation of Emission Level Goals has evolved during the course of the MEG's project and is significantly different from the initial chart introduced some 18 months ago. Elimination of Discharge, as a criteria for Emission Level Goals, was added about a year ago. In another interim version, columns specifying dilution factors in multiples of ten were included under the Emission Level Goals based on ambient factors. Later, Minimum Acute Toxicity Effluents (MATE's) were incorporated and the dilution factor columns deleted. It is likely that the chart will be further altered as the MEG's become more refined, but the format presented here serves well for displaying MEG's at this stage of development.

Ambient Level Goals

The lower half of the MEG's chart is designed to present three classifications of Ambient Level Goals; all of these goals describe estimated permissible concentrations (EPC's) for continuous exposure. The Ambient Level Goals presented in the chart are those based on:

1) Current or proposed Federal ambient standards or criteria.
2) Toxicity (acute and chronic effects considered).
3) Carcinogenicity or teratogenicity (for zero threshold pollutants).

The term zero threshold pollutants is used to distinguish contaminants demonstrated to be potentially carcinogenic or teratogenic. The concept of thresholds is based on the premise that there exists for every chemical substance, some defineable concentration below which that chemical will not produce a toxic response in an exposed subject.[3] The existence of thresholds for carcinogens, teratogens, and mutagens has been widely debated and is still unresolved. In using the term "zero threshold pollutants," we do not wish to imply that we have chosen sides in the debate; rather, we use the nomenclature as a convenience.

BACKGROUND INFORMATION SUMMARIES FOR CHEMICAL SUBSTANCES

An obvious need in the field of environmental assessment has been for a useable instrument bringing together data related to environmental aspects of various chemical substances. The format developed for supplying summarized background information to accompany and substantiate MEG's charts addresses this need, providing a large volume of information in a consolidated, consistent, workable arrangement. This format serves to organize available data in a logical framework, yet at the same time remains flexible enough to allow incorporation of data as it becomes available. Specific items of information are arranged in a consistent pattern, and presented in conjunction with the corresponding MEG's chart. This allows the user to survey the data quickly and to relate multimedia environmental goals to physical and chemical properties, and toxicological characteristics of the chemical substance of interest.

Space is provided on each Background Information Summary to supply the following types of data:

- Identifying Information
- Properties
- Natural Occurrence, Characteristics, Associated Compounds
- Toxic Properties, Health Effects
- Regulatory Actions, Standards, Criteria, Candidate Status for Specific Regulation

Table 1 lists the specific items of information included in the Background Information Sum-

TABLE 1

INFORMATION PRESENTED IN BACKGROUND INFORMATION SUMMARIES

General Heading	Specific Items
IDENTIFYING INFORMATION	Category number, Preferred name, Synonyms, Empirical chemical formula, Structure, Wiswesser Line Notation, Physical description
PROPERTIES	Molecular or atomic weight, Atomic number Periodic group, Boiling point, Melting point, Density, Vapor density, Vapor pressure, Dissociation constant
NATURAL OCCURENCES, CHARACTERISTICS, AND ASSOCIATED COMPOUNDS	Background levels in air, Odor levels, Photochemical activity, Background levels in water, Occurence associations, Dietary intake, Characteristic chemical reactions, Metabolic fate, Background levels in soil
TOXIC PROPERTIES AND HEALTH EFFECTS	Animal toxicity information: LD_{50} - lethal dose (50% kill) LC_{50} - lethal concentration (50% kill) LD_{Lo} - lowest published lethal dose LC_{Lo} - lowest published lethal concentration Human health effects data: acute effects, chronic effects, biological half-life Data pertinent to carcinogenicity or teratogenicity: EPA/NIOSH ordering number, Affected animal species, Recorded human effects, Lowest effective dosages, Adjusted ordering number Aquatic toxicity information: LC_{50} - lethal concentration (50% kill) Bioaccumulation, or biomagnification (potential), Reported tainting levels, Phytotoxicity (plant toxicity) data
REGULATORY ACTIONS, STANDARDS, CRITERIA, RECOGNITION AND CANDIDATE STATUS FOR SPECIFIC REGULATIONS	National Primary and Secondary Ambient Air Quality Standards (40 CFR, Part 50). National Emissions Standards for Hazardous Air Pollutants (40 CFR, Part 61). OSHA Standards for Hazardous Substances (29 CFR, Part 1910). National Interim Primary Drinking Water Regulations (40 CFR, Part 141). Public Health Service Drinking Water Standards (42 CFR, Part 72). EPA Toxic Pollutant Effluent Standards (40 CFR, Part 405-460). Regulations for Protection Against Radiation (10 CFR, Part 20). FDA Declaration EPA National Emissions Standards for Hazardous Air Pollutants, Candidate List. EPA Toxic Pollutant Effluent Standards, Candidate List. EPA Consent Decree List. NCI List of Carcinogens to Man. ACGIH designation as carcinogen, simple asphyxiant, or nuisance particulate. EPA Star Document subject. NIOSH Criteria Document subject. Chemical Industry Institute of Toxicology Priority Chemical Lists.

maries under each of these headings. In addition to these items, calculations of MATE's and EPC's are also presented in the summaries.

MEG' METHODOLOGY

A methodology for evaluating and ranking pollutants for the purpose of environmental assessment, has been developed which can be used to delineate MEG's for a large number of compounds. The system requires certain empirical data which are extrapolated through simple models to yield EPC's or MATE's. The methodology addresses both Ambient Level Goals and Emission Level Goals based on ambient factors.

Existing or proposed Federal standards, criteria, or recommendations are acknowledged as previously established goals and have been utilized wherever applicable. For those substances not addressed by current guidelines, consideration in arriving at MEG's goals has been given to the following: (1) established or estimated human threshold levels; (2) acceptable risk levels for lifetime exposure to suspected carcinogens or teratogens; (3) degrees of contamination considered reasonable for protection of existing ecosystems; (4) cumulative potential in aquatic organisms, livestock, and vegetation; and (5) hazards to human health or to ecology induced by short term exposure to emissions. It is recognized that there are several other criteria pertinent to MEG's that have not been incorporated into the methodology developed thus far (for example, quality of the receiving media before introduction of the substance, characteristics of transport and dispersion of emissions, consideration of location and abundance of sources emitting a given pollutant, numbers of populations affected, synergisms, antagonisms, and other secondary pollutant associations); new research is needed before more refined models of estimation can be developed to allow inclusion of these criteria.

Three distinct aspects of MEG's methodology development have been addressed so far. These are:

1) assembling and collating all existing or proposed Federal guidelines pertinent to each chemical substance on the Master List.
2) defining models to translate empirical data into EPC's) estimated permissible concentrations for continuous exposure to chemical toxicants in air, water, and land).
3) defining models to translate empirical data into values describing MATE's (minimum acute toxicity effluents safe for short term exposure; such effluents may be gases, liquids, or solids).

Federal Guidelines

Investigation of Federal Guidelines has yielded not only values to serve as MEG's, but also insight into the variety of approches applied in standard setting thus far. For example, the National Emissions Standards for Hazardous Air Pollutants established for mercury and beryllium take into consideration estimated safe ambient levels of these pollutants (1 $\mu g/^3$ for Hg, 0.01 $\mu g/m^3$ for Be).[4] Emission guidelines may be expressed in many different units such as the ratio of mass or volume of pollutant to the mass of feedstock or product. Ambient guidelines may also be expressed in units other than concentration units, for example, certain water quality criteria for protection of aquatic life specify application factors to be applied to the 96-hr LC_{50}.

Existing Federal Guidelines fall far short of providing MEG's for all the chemical substances of concern. In fact, our survey of the Federal guidelines showed only about 40 specific contaminants receive attention by more than one set of emissions or ambient guidelines. The MEG's list, as mentioned earlier, includes more than 600 specific chemical substances.

Estimated Permissible Concentrations (EPC's)

To delineate Multimedia Environmental Goals a defined frame of reference for each substance must be established as a common reference point to allow comparison of various characteristics among similar and diverse substances. Translation of various forms of data into EPC's meets this need.

Two types of EPC's are generated through modeling. Empirical data concerning the effects of chemical substances on human health and the ecology are translated into a set of toxicity-based EPC's. Another set of EPC's is supplied by a system relating carcinogenic or teratogenic potential to media concentrations considered to pose an acceptable risk.

The methodology defines a total of 22 different kinds of EPC's, many of them interrelated (EPC's for water, for example, may be derived from EPC's for air). Although multiple EPC's are calculated on the background information summaries, only the most stringent EPC for a given media/criteria combination will appear on the MEG chart for a given substance.

EPC's have been coded by subscripts for easy identification. EPC_{AHI}, for example, is the toxicity based EPC for air based on human health effects (derived from air model #1); EPC_{WEI} applies to water and is based on ecological effects (water model #1 is used); EPC_{ACI} is for air and is based on carcinogenic potential (established by carcinogen model #1).

Several of the models incorporated were developed or suggested by previous researchers; other models were designed or modified specifically for MEG's application. The significance of the methodology lies not in any specific model, but in the array of models which allows MEG's to be defined on the basis of a variety of data items. Empirical data required for the various health based EPC's and interrelationships defined in the methodology are listed in Table 2. EPC's based on ecological effects are defined in Table 3. Most specific types of data required have been compiled previously by others and are largely available in tabulated form within secondary sources of information.

Minimum Acute Toxicity Effluents (MATE's)

The system established to describe MATE values as Emission Level Goals is analogous to that developed for EPC's. The basic difference is that the MATE's refer to concentrations appropriate for short term exposure whereas EPC's consider lifetime continuous exposure. Fourteen different kinds of MATE values are defined currently.

APPLICATION OF METHODOLOGY FOR DESCRIBING MEG's

Presentation in detail of all the models supporting the EPC and MATE derivations is beyond the scope of this paper. However, a few general comments are required to permit some perspective into the methodology. First, all of the modeling schemes require that certain assumptions be made and a worst case approach has been taken to keep the MEG values conservative. In some instances, arbitrary constants are incorporated in an effort to correlate the various sets of EPC's. Efforts have been made to incorporate judgments of others relative to the levels of pollutants safely tolerated by human beings. In this regard, heavy reliance in the methodology has been placed on TLV's established by the American Conference of Governmental Industrial Hygienists (ACGIH).[5]

So far, 216 chemical substances from the MEG's Master List have been addressed utilizing the previously described format and methodology. While the rapid increase in volume of data accessible in recent months has increased the reliability of assessment schemes based on modeling techniques, data gaps remain a problem over a wide range of the entries. These gaps make it impossible to provide, for every substance addressed, goals for each medium on the basis of all the applicable models. However, when provision is made for utilizing data in a variety of forms, it becomes possible to describe MEG's which are reasonable based on at least some of the selected criteria. As a result of this adaptability, the methodology provides a practical, workable system for determining goals in an ever increasing percentage of cases. Of the 216 substances addressed, only 6 emerge with no numerical MEG values, providing a good indication that the methodology is sufficiently broad in its bases to provide the comparison criteria needed for environmental assessment.

Six samples taken from the MEG's compilations follow the text.

TABLE 2

DERIVATION OF HEALTH BASED EPC's

Data	Interrelationship	Specific EPC Derived
TLV or NIOSH Recommendation (occupational exposure)		EPC_{AH1}, EPC_{AC1}
LD_{50}, LD_{Lo}	$TLV \propto LD_{50}$*	EPC_{AH2}
Bioassay data (carcinogen testing)		EPC_{AC2}
Bioassay data (teratogen testing)		EPC_{AT}
	$EPC_{WH} \propto EPC_{AH}$**	EPC_{WH1}
LD_{50}		EPC_{WH2}
	$EPC_{WC} \propto EPC_{AC}$**	EPC_{WC}
	$EPC_{WT} \propto EPC_{AT}$**	EPC_{WT}
	$EPC_{LH} \propto EPC_{WH}$	EPC_{LH}
	$EPC_{LC} \propto EPC_{WC}$	EPC_{LC}
	$EPC_{LT} \propto EPC_{WT}$	EPC_{LT}

* Relationship established by Handy and Schindler.[6]

** Relationship suggested by Stokinger and Woodward.[7]

Subscript Key: A (air); W (water); L (land); H (health effects); C (carcinogenicity); T (teratogenicity); numbers refer to specific models.

TABLE 3

DERIVATION OF ECOLOGY BASED EPC's

Data	Interrelationship	Specific EPC Derived
Air concentration causing an effect in vegetation		EPC_{AE}
LC_{50} or TLm		EPC_{WE1}
Tainting Level		EPC_{WE2}
Cumulative Potential		EPC_{WE3}
Application Factor*		EPC_{WE4}
Hazard Level*		EPC_{WE4}
	$EPC_{LE} \propto EPC_{WE}$	EPC_{LE}

* Value supplied in Water Quality Criteria

Subscript Key: A (air); W (water); L (land); E (ecological effects); numbers refer to specific models.

CONCLUSIONS

The MEG's project represents an important step in EPA's efforts to systematically address a multiplicity of chemical substances for the purpose of establishing priorities in environmental assessment programs. MEG's provide a ranking system furnishing the decision criteria needed in source assessment. The MEG's may also be used for establishing priorities among the pollutants to be ultimately addressed by regulations, and thus, may influence control technology development in the future. In every case care has been taken to arrive at conservative but reasonable figures based upon the array of possible options supplied by the methodology.

It is expected that this initial work addressing Multimedia Environmental Goals will provide a springboard for further research in developing MEG's and that it will stimulate exploration into more sophisticated approaches that make use of empirical data evolving from research efforts currently in progress.

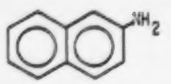
REFERENCES

1. Environmental Protection Agency. Quality Criteria for Water. EPA 440/9/76-023 (1976).
2. Environmental Protection Agency. Standards of Performance for New Stationary Sources, Title 40 Code Federal Regulations Part 60.
3. Herbert E. Stokinger. Concepts of Thresholds in Standards Setting. Arch Environ Health, 25 (Sept. 1972), 153.
4. Environmental Protection Agency. National Hazardous Emissions Standards for Hazardous Air Pollutants. Federal Register, 36, 234, (Dec. 7, 1971), 23239.
5. American Conference of Governmental Industrial Hygienists. Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Hygienists, Cincinnati, Ohio (1976).
6. R. Handy and A. Schindler. Estimation of Permissible Concentration of Pollutants for Continuous Exposure. Prepared by Research Triangle Institute under Contract 68-02-1325 for Environmental Protection Agency Research Triangle Park, N.C. EPA-600 12-76-155 (1976).
7. Herbert E. Stokinger and Richard L. Woodward. Toxicologic Methods for Establishing Drinking Water Standards. Journal of American Water Works Association, 515 (1958), 515.

CATEGORY: 10C

WLN: L66J CZ

STRUCTURE:



2-AMINONAPHTHALENE: $C_{10}H_9N$ (2-naphthylamine, β-naphthylamine).
White crystals that darken on exposure to light and air; volatile with steam.

PROPERTIES:

Molecular wt: 143.19; mp: 113; bp: 306; d: 1.0614^{98}_{4}; vap. press.: 1 mm at 108° C; volatile in steam; slightly soluble in cold water.

NATURAL OCCURRENCE, CHARACTERISTICS, ASSOCIATED COMPOUNDS:

2-Naphthylamine does not occur as such in nature, but is formed by the pyrolisis of nitrogen-containing organic matter. It has been isolated from coal-tar (ref. 44). It has, in general, the characteristics of primary aromatic amines. It is a weak base.

TOXIC PROPERTIES, HEALTH EFFECTS:

Epidemiological studies have shown that occupational exposure to 2-aminonaphthalene is strongly associated with the occurrence of bladder cancer. There is no doubt that the compound is a human bladder carcinogen (ref. 44). 2-Aminonaphthalene is also reported to cause cancer in several animal species.

The EPA/NIOSH ordering number is 7628. The lowest dose to induce a carcinogenic response is reported as 18 mg/kg. The adjusted ordering number is 423.8.

LD_{50} (oral, rat): 727 mg/kg.

Aquatic toxicity: TLm 96: 10-1 ppm (ref. 2).

REGULATORY ACTIONS, STANDARDS, CRITERIA, RECOGNITION, CANDIDATE STATUS FOR SPECIFIC REGULATION:

2-Aminonaphthalene is recognized by ACGIH as a carcinogenic agent in humans. No TLV has been assigned.

β-Naphthylamine was the subject of a NIOSH Hazard Review Document (ref. 43).

OSHA standards dealing with exposure of employees to 2-naphthylamine has been established taking into consideration substantial evidence that 2-naphthylamine is known to cause cancer (ref. 17).

MINIMUM ACUTE TOXICITY CONCENTRATIONS:

Air, Health: $7 \times 10^4/423.8 = 165$ μg/m^3
Water, Health: $15 \times 165 = 2.5 \times 10^3$ μg/ℓ
Land, Health: $0.002 \times 2.5 \times 10^3 = 5$ μg/g

Air, Ecology:
Water, Ecology: $100 \times 1 = 100$ μg/ℓ
Land, Ecology: $0.002 \times 100 = 0.2$ μg/g

ESTIMATED PERMISSIBLE CONCENTRATIONS:

$EPC_{AH2} = 0.107 \times 727 = 78$ μg/m^3
$EPC_{AH3} = 0.081 \times 727 = 59$ μg/m^3
$EPC_{WH1} = 15 \times 59 = 3{,}500$ μg/ℓ
$EPC_{WH2} = 0.4 \times 727 = 291$ μg/ℓ
$EPC_{LH} = 0.002 \times 291 = 0.6$ μg/g
$EPC_{AC2} = 10^3/(6 \times 423.8) = 0.4$ μg/m^3
$EPC_{WC} = 15 \times 0.4 = 6$ μg/ℓ
$EPC_{LC} = 0.002 \times 6 = 0.012$ μg/g

$EPC_{WE1} = 50 \times 1 = 50$ μg/ℓ
$EPC_{LE} = 0.002 \times 50 = 0.1$ μg/g

MULTIMEDIA ENVIRONMENTAL GOALS

X
10C
2-AMINONAPHTHALENE

EMISSION LEVEL GOALS							
	I. Based on Best Technology		II. Based on Ambient Factors				
	A. Existing Standards	B. Developing Technology	A. Minimum Acute Toxicity Effluent		B. Ambient Level Goal*		C. Elimination of Discharge
	NSPS, BPT, BAT	Engineering Estimates (R&D Goals)	Based on Health Effects	Based on Ecological Effects	Based on Health Effects	Based on Ecological Effects	Natural Background*
Air, μg/m³ (ppm Vol)			1.65E2		0.4		
Water, μg/l (ppm Wt)			2.5E3	1.0E2	6	50	
Land, μg/g (ppm Wt)			5.0E0	2.0E-1	0.012	0.1	

*To be multiplied by dilution factor

AMBIENT LEVEL GOALS					
	I. Current or Proposed Ambient Standards or Criteria		II. Toxicity Based Estimated Permissible Concentration		III. Zero Threshold Pollutants Estimated Permissible Concentration
	A. Based on Health Effects	B. Based on Ecological Effects	A. Based on Health Effects	B. Based on Ecological Effects	Based on Health Effects
Air, μg/m³ (ppm Vol)			59		0.4
Water, μg/l (ppm Wt)			291	50	6
Land, μg/g (ppm Wt)			0.6	0.1	0.012

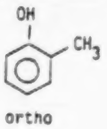
CATEGORY: 18A

WLN:

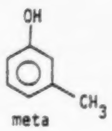
CRESOLS: $C_6H_4OHCH_3$ (cresylic acid, methylphenol, hydroxytoluene).

m-cresol: colorless or yellowish liquid, phenolic odor;
o-cresol: crystals or liquid, phenolic odor;
p-cresol: crystals, phenolic odor.

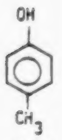
STRUCTURE:



ortho



meta



para

PROPERTIES:

Molecular wt: 108.37; density$^{4}_{20}$: 1.034-1.047;
vap. d: 3.72; soluble in water.

	mp	bp	vap. press.
m-cresol	11	202	0.153 mm at 25°C
o-cresol	30	191	0.245 mm at 25°C
p-cresol	35.5	201.8	0.108 mm at 25°C

NATURAL OCCURRENCE, CHARACTERISTICS, ASSOCIATED COMPOUNDS:

Cresols are methyl-substituted hydroxy benzene compounds, i.e. methyl phenols. Ortho, meta and para compounds occur. The meta isomer predominates in mixtures (ref. 24)

Odor recognition level for cresols ranges from 0.9 to 1.21 mg/m^3 or 0.20 to 0.27 ppm (ref. 3).

The odor threshold in air for p-cresol is reported as 0.001 ppm or 4 µg/m^3 (ref. 29).

Cresols are obtained from coal tar (ref. 24). Due to the low vapor pressure and disagreeable odor, cresols usually do not present an acute inhalation hazard (ref. 63).

Cresols are highly resistant to biological oxidation (ref. 67).

TOXIC PROPERTIES, HEALTH EFFECTS:

Toxic properties of cresols are similar to those of phenol. Cresols may be absorbed through the skin. Respiratory hazard is low because of low volatility. Absorption may cause damage to liver, kidney and nervous system (ref. 9). Order of toxicity beginning with most toxic is reported to be as follows: p-cresol; o-cresol; phenol; m-cresol (ref. 4)

	LD_{50} (oral, rat)
m-cresol	242 mg/kg
o-cresol	121 mg/kg
p-cresol	207 mg/kg

Toxicity to aquatic life: tainting of fish may result from concentrations of 0.07 mg/ℓ of mixed cresol isomers (ref. 28). The toxic concentration of p-cresol is 5 ppm for rainbow trout (ref. 36). The 96-hour LC_{50} for p-cresol is reported as 19 mg/ℓ (ref. 68). For mixed cresol isomers, the 96-hour TLm is reported as 10-1 ppm (ref. 2).

REGULATORY ACTIONS, STANDARDS, CRITERIA, RECOGNITION, CANDIDATE STATUS FOR SPECIFIC REGULATION:

TLV for Cresol (all isomers): 22 mg/m^3 (5 ppm).

EPA 1976 Water Quality Criteria (proposed): 1 µg/ℓ of phenol (including phenolic compounds) for domestic water supply (welfare) and to protect against fish flesh tainting (ref. 33).

NAS/NAE 1972 Water Quality Criteria: 1 µg/ℓ of phenolic compounds in public water supply sources to prevent odor from chlorinated phenols. To prevent tainting and toxic effects in aquatic life: Concentration no greater than 100 µg/ℓ at any time or place; application factor of 0.05 (for phenols) (ref. 28).

U.S. Public Health Service Drinking Water Regulations, 1962--Levels for alternate source selection: 1 µg/ℓ (for phenols) (ref. 66).

MINIMUM ACUTE TOXICITY CONCENTRATIONS:

Air, Health: 2.2 x 10^4 µg/m^3 (5 ppm)
Water, Health: 5 x 1 = 5 µg/ℓ
Land, Health: 0.002 x 5 = 0.01 µg/g

Air, Ecology:
Water, Ecology: 100 x 5 = 500 µg/ℓ
Land, Ecology: 0.002 x 500 = 1 µg/g

ESTIMATED PERMISSIBLE CONCENTRATIONS:

EPC_{AH1} = 10^3 x 22/420 = 52 µg/m^3
EPC_{AH1a} = 5/420 = 0.01ppm
EPC_{WH1} = 15 x 52 = 780 µg/ℓ
EPC_{WH2} = 13.8 x 22 = 304 µg/ℓ
EPC_{WHS} = 1 µg/ℓ (phenolic compounds)
EPC_{LH} = 0.002 x 1 = 0.002 µg/g

EPC_{WE1} = 50 x 1 = 50 µg/ℓ
EPC_{WE2} = 70 µg/ℓ
EPC_{WES} = 100 µg/ℓ (phenolic compounds)
EPC_{LE} = 0.002 x 50 = 0.1 µg/g

18A
CRESOLS

EMISSION LEVEL GOALS							
	I. Based on Best Technology		II. Based on Ambient Factors				
	A. Existing Standards	B. Developing Technology	A. Minimum Acute Toxicity Effluent		B. Ambient Level Goal*		C. Elimination of Discharge
	NSPS, BPT, BAT	Engineering Estimates (R&D Goals)	Based on Health Effects	Based on Ecological Effects	Based on Health Effects	Based on Ecological Effects	Natural Background*
Air, μg/m^3 (ppm Vol)			2.2E4		52 (0.01)		
Water, μg/l (ppm Wt)			5.0E0	5.0E2	1	70	
Land, μg/g (ppm Wt)			1.0E-2	1.0E0	0.002	0.1	

*To be multiplied by dilution factor

AMBIENT LEVEL GOALS					
	I. Current or Proposed Ambient Standards or Criteria		II. Toxicity Based Estimated Permissible Concentration		III. Zero Threshold Pollutants Estimated Permissible Concentration
	A. Based on Health Effects	B. Based on Ecological Effects	A. Based on Health Effects	B. Based on Ecological Effects	Based on Health Effects
Air, μg/m^3 (ppm Vol)			52 (0.01)		
Water, μg/l (ppm Wt)	1†	100†	304	50	
Land, μg/g (ppm Wt)			0.002	0.1	

†Phenolic compounds.

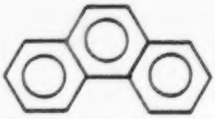
CATEGORY: 21

WLN: LB666J

PHENANTHRENE: $C_{14}H_{10}$.

Monoclinic crystals from alcohol; solutions exhibit faint blue fluorescence.

STRUCTURE:



PROPERTIES:

Molecular wt: 178; mp: 101; bp: 340; d: 0.9800^4; vap. press.: 1 mm at 118.3; vap. d: 6.14; insoluble in water; solubility may be enhanced by surfactant impurities in water (ref. 58); lipid solubility: 2 percent solution in olive oil (ref. 72).

NATURAL OCCURRENCE, CHARACTERISTICS, ASSOCIATED COMPOUNDS:

Phenanthrene is among the lower molecular weight polycyclic hydrocarbons comprising the volatile portion of the benzene-soluble fraction of coal tar (ref. 4). Concentrations of 0.6102 µg/1,500 m^3 and 6 µg/1,000 m^3 in urban air are reported (ref. 1). This is equivalent to 0.0004 to 0.006 µg/m^3. Phenanthrene is associated with particulate polycvclic aromatic hydrocarbons, PPAH, (ref. 71). The following concentrations of PPAH have been estimated or reported: Air (urban environment in winter in seven selected U.S. cities): 21.6 ng/m^3 - 146 ng/m^3 (ref. 71); groundwater and surface-treated water: 0.001 µg/ℓ - 0.025 µg/ℓ (ref. AAS); upper layer of Earth's crust: 100 µg/kg - 1,000 µg/kg (ref. 58).

TOXIC PROPERTIES, HEALTH EFFECTS:

LD_{50} (oral, mouse): 700 mg/kg.

Phenanthrene may be present in soot, coal tar, and pitch, which are known to be carcinogenic to man. Carcinogenic polycyclic aromatic hydrocarbons may induce tumors at the site of application (ref. 59). Phenanthrene is included in the NIOSH Suspected Carcinogens List. The EPA/NIOSH ordering number is 3121. The lowest dose to induce an oncogenic response is reported as 71 mg/kg. The adjusted ordering number is 44.

REGULATORY ACTIONS, STANDARDS, CRITERIA, RECOGNITION, CANDIDATE STATUS FOR SPECIFIC REGULATION:

Phenanthrene appears on EPA Consent Decree List with an assigned priority of 1.

TLV (coal-tar pitch volatiles): 0.2 mg/m^3. [The specification includes naphthalene, anthracene, acridine, phenanthrene, and fluorene, collectively. The purpose of the TLV is to minimize concentrations of higher weight polycyclic hydrocarbons which are carcinogenic (ref. 4)].

MINIMUM ACUTE TOXICITY CONCENTRATIONS:

Air, Health: $7 \times 10^4/44 = 1.59 \times 10^3$ µg/m^3

Water, Health: $15 \times 1.59 \times 10^3 = 2.39 \times 10^4$ µg/ℓ

Land, Health: $0.002 \times 2.39 \times 10^4 = 47.8$ µg/g

Air, Ecology:

Water, Ecology:

Land, Ecology:

ESTIMATED PERMISSIBLE CONCENTRATIONS:

$EPC_{AH2} = 0.107 \times 700 = 75$ µg/m^3

$EPC_{AH3} = 0.081 \times 700 = 57$ µg/m^3

$EPC_{WH1} = 15 \times 57 = 855$ µg/ℓ

$EPC_{WH2} = 0.4 \times 700 = 280$ µg/ℓ

$EPC_{LH} = 0.002 \times 280 = 0.56$ µg/g

$EPC_{AC2} = 10^3/(6 \times 44) = 3.8$ µg/m^3

$EPC_{WC} = 15 \times 3.9 = 57$ µg/ℓ

$EPC_{LC} = 0.002 \times 57 = 0.114$ µg/g

MULTIMEDIA ENVIRONMENTAL GOALS

21

PHENANTHRENE

EMISSION LEVEL GOALS

	I. Based on Best Technology		II. Based on Ambient Factors				
	A. Existing Standards	B. Developing Technology	A. Minimum Acute Toxicity Effluent		B. Ambient Level Goal*		C. Elimination of Discharge
	NSPS, BPT, BAT	Engineering Estimates (R&D Goals)	Based on Health Effects	Based on Ecological Effects	Based on Health Effects	Based on Ecological Effects	Natural Background*
Air, $\mu g/m^3$ (ppm Vol)			1.59E3		3.8		
Water, $\mu g/l$ (ppm Wt)			2.39E4		57		
Land, $\mu g/g$ (ppm Wt)			4.8E1		0.114		

*To be multiplied by dilution factor

AMBIENT LEVEL GOALS

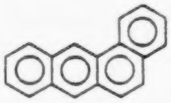
	I. Current or Proposed Ambient Standards or Criteria		II. Toxicity Based Estimated Permissible Concentration		III. Zero Threshold Pollutants Estimated Permissible Concentration
	A. Based on Health Effects	B. Based on Ecological Effects	A. Based on Health Effects	B. Based on Ecological Effects	Based on Health Effects
Air, $\mu g/m^3$ (ppm Vol)			57		3.8
Water, $\mu g/l$ (ppm Wt)			280		57
Land, $\mu g/g$ (ppm Wt)			0.56		0.114

CATEGORY: 21

WLN: L D6 B666J

BENZ(a)ANTHRACENE: $C_{18}H_{12}$ (benzo(b)phenanthrene, 1,2-benzanthracene, 2,3-benzophenanthrene, BA). Crystallizes in the form of plates from ethanol. Solutions exhibit greenish-yellow fluorescence.

STRUCTURE:



PROPERTIES:

Molecular wt.: 228.28; mp: 158-9; bp: 400° C; sublimes; insoluble in water; solubility may be enhanced by surfactant impurities in water (ref. 58); lipid solubility: 0.6 mg/0.2 ml neutral, sterile olive oil (ref. 72).

NATURAL OCCURRENCE, CHARACTERISTICS, ASSOCIATED COMPOUNDS:

Benz(a)anthracene occurs in coal car and is associated with particulate polycyclic aromatic hydrocarbons, PPAH. The lowest urban air concentration reported for benz(a)anthracene is 44.69 $\mu g/m^3$ (ref. 1). This is equivalent to 0.029 $\mu g/m^3$.

Concentrations of BA in soils (nonindustrial areas) ranging from 5-20 $\mu g/kg$ have been reported (ref. 73).

Other concentrations of BA are reported as follows: (a) drinking water - 23.2 $\mu g/m^3$; (b) cooked meat or fish - 189 $\mu g/kg$; (c) vegetables - 230 $\mu g/kg$; (d) roasted coffee - 14.2 $\mu g/kg$ (ref. 73).

TOXIC PROPERTIES, HEALTH EFFECTS:

LD_{Lo} (intravenous, mouse): 10 mg/kg.

Benz(a)anthracene may be present in soot, coal tar, and pitch, which are known to be carcinogenic to man. Carcinogenic polycyclic aromatic hydrocarbons may induce tumors at the site of application (ref. 59). Benz(a)anthracene is included in the NIOSH Suspected Carcinogens List. The EPA/NIOSH ordering number is 3124. The lowest dose to induce a carcinogenic response is reported as 2 mg/kg. The adjusted ordering number is 1562.

REGULATORY ACTIONS, STANDARDS, CRITERIA, RECOGNITION, CANDIDATE STATUS FOR SPECIFIC REGULATION:

TLV = 0.2 mg/m^3 [for particulate polycyclic aromatic hydrocarbons (PPAH). This TLV recognizes the carcinogenic potential of PPAH collectively].

Benz(a)anthracene appears on the EPA Consent Decree List with an assigned priority of 1.

MINIMUM ACUTE TOXICITY CONCENTRATIONS:

Air, Health: $7 \times 10^4/1{,}562 = 44.8\ \mu g/m^3$
Water, Health: $15 \times 44.8 = 672\ \mu g/\ell$
Land, Health: $0.002 \times 672 = 1.34\ \mu g/g$

Air, Ecology:
Water, Ecology:
Land, Ecology:

ESTIMATED PERMISSIBLE CONCENTRATIONS:

$EPC_{AH2} = 0.107 \times 10 = 1.07\ \mu g/m^3$
$EPC_{AH3} = 0.081 \times 10 = 0.81\ \mu g/m^3$
$EPC_{WH1} = 15 \times 0.81 = 12.2\ \mu g/\ell$
$EPC_{WH2} = 0.4 \times 10 = 4.0\ \mu g/\ell$
$EPC_{LH} = 0.002 \times 4 = 0.008\ \mu g/g$
$EPC_{AC2} = 10^3/(6 \times 1{,}562) = 0.11\ \mu g/m^3$
$EPC_{WC} = 15 \times 0.11 = 1.65\ \mu g/\ell$
$EPC_{LC} = 0.002 \times 1.65 = 0.003\ \mu g/g$

MULTIMEDIA ENVIRONMENTAL GOALS

XX
21
BENZ(a)ANTHRACENE

EMISSION LEVEL GOALS							
	I. Based on Best Technology		II. Based on Ambient Factors				
	A. Existing Standards	B. Developing Technology	A. Minimum Acute Toxicity Effluent		B. Ambient Level Goal*		C. Elimination of Discharge
	NSPS, BPT, BAT	Engineering Estimates (R&D Goals)	Based on Health Effects	Based on Ecological Effects	Based on Health Effects	Based on Ecological Effects	Natural Background*
Air, $\mu g/m^3$ (ppm Vol)			4.5E1		0.11		0.029+
Water, $\mu g/l$ (ppm Wt)			6.7E2		1.65		0.023‡
Land, $\mu g/g$ (ppm Wt)			1.3E0		0.003		0.02

*To be multiplied by dilution factor

AMBIENT LEVEL GOALS					
	I. Current or Proposed Ambient Standards or Criteria		II. Toxicity Based Estimated Permissible Concentration		III. Zero Threshold Pollutants Estimated Permissible Concentration
	A. Based on Health Effects	B. Based on Ecological Effects	A. Based on Health Effects	B. Based on Ecological Effects	Based on Health Effects
Air, $\mu g/m^3$ (ppm Vol)			0.81		0.11
Water, $\mu g/l$ (ppm Wt)			4.0		1.65
Land, $\mu g/g$ (ppm Wt)			0.008		0.003

+Reported for urban air. No rural concentration is reported.

‡Drinking water.

CATEGORY: 54

HYDROGEN SELENIDE. H_2Se (selenium hydride).

Colorless poisonous gas; disagreeable odor of decayed horseradish.

WLN: H2 SE

STRUCTURE:

H_2Se

PROPERTIES:

Molecular wt: 80.98; mp: -60.4; bp: -41.5; gas density: 3.664^{760} (air); vap. press: 10 atm at 23.4° C; solubility (in water: 270 mℓ/100 mℓ at 22.5°.

NATURAL OCCURRENCE, CHARACTERISTICS, ASSOCIATED COMPOUNDS:

Hydrogen selenide is formed by the action of dilute acids on metallic selenides. Selenium will combine directly with hydrogen at temperatures below 250° C to form H_2Se. Hydrogen selenide unites directly with most metals to form metal selenides. The odor recognition level for hydrogen selenide is 1.00 mg/m^3 (ref. 3). Hydrogen selenide gas is important as an air contaminant. Because the gas is highly soluble in water, it is also a potential water contaminant.

TOXIC PROPERTIES, HEALTH EFFECTS:

Systemic poisoning as well as pulmonary irritation may result from exposure to hydrogen selenide. Liver damage is reported from exposed experimental animals (ref. 4). It is generally considered to be more toxic than elemental selenium. The lowest toxic dose affecting the central nervous system of a human is 0.2 ppm. See also Selenium and Selenium Compounds.

LC_{50} (inhalation, guinea pig): 1 mg/m^3/8 hr.

REGULATORY ACTIONS, STANDARDS, CRITERIA, RECOGNITION, CANDIDATE STATUS FOR SPECIFIC REGULATION:

TLV = 0.2 mg/m^3 (0.05 ppm).

Standards and criteria applicable to selenium compounds include the following:

Selenium is a candidate for the list for Toxic Pollutant Effluent Standards (ref. 10). It is included in the EPA Consent Decree List, Priority III.

National Interim Primary Drinking Water Standards: 0.01 mg/ℓ, as Se (ref. 102).

U.S. Public Health Service Drinking Water Standards, Levels for Source Rejection: 0.01 mg/ℓ, as Se (ref. 66).

EPA 1976 Water Quality Criteria (proposed): For domestic water supply (health)--10 μg/ℓ; for marine and freshwater aquatic life--application factor: 0.01 (to be applied to 96-hr LC_{50}) (ref. 33).

NAS/NAE Water Quality Criteria, 1972: For public water supply sources--0.01 mg/ℓ for marine aquatic life: hazard level--0.01 mg/ℓ; minimal risk of deleterious effects--0.005 mg/ℓ; application factor--0.01 (to be applied to the 96-hr LC_{50}); for livestock--0.05 mg/ℓ; for irrigation--0.02 mg/ℓ for continuous use on all soils (ref. 28).

MINIMUM ACUTE TOXICITY CONCENTRATIONS:

Air, Health: 200 $\mu g/m^3$ (0.05 ppm)
Water, Health: 5 x 10 = 50 μg/ℓ, as Se
Land, Health: 0.002 x 50 = 0.1 μg/g, as Se

Air, Ecology:
Water, Ecology: 5 x 5 = 25 μg/ℓ, as Se
Land, Ecology: 0.002 x 25 = 0.05 μg/g, as Se

ESTIMATED PERMISSIBLE CONCENTRATIONS:

$EPC_{AH1} = 10^3 \times 0.2/420 = 0.5\ \mu g/m^3$
$EPC_{AH1a} = 0.05/420 = 0.0001$ ppm
$EPC_{WH1} = 15 \times 0.5 = 7.5\ \mu g/\ell$
$EPC_{WH2} = 13.8 \times 0.2 = 2.8\ \mu g/\ell$
$EPC_{WHS} = 10\ \mu g/\ell$
$EPC_{LH} = 0.002 \times 10 = 0.02\ \mu g/g$

$EPC_{WES} = 5\ \mu g/\ell$
$EPC_{LE} = 0.002 \times 5 = 0.01\ \mu g/g$

MULTIMEDIA ENVIRONMENTAL GOALS

XX
54
HYDROGEN SELENIDE

EMISSION LEVEL GOALS							
	I. Based on Best Technology		II. Based on Ambient Factors				
	A. Existing Standards	B. Developing Technology	A. Minimum Acute Toxicity Effluent		B. Ambient Level Goal*		C. Elimination of Discharge
	NSPS, BPT, BAT	Engineering Estimates (R&D Goals)	Based on Health Effects	Based on Ecological Effects	Based on Health Effects	Based on Ecological Effects	Natural Background*
Air, μg/m³ (ppm Vol)			2.0E2 (0.05)		0.5 (0.0001)		
Water, μg/l (ppm Wt)			5.0E1	2.5E1	10	5	
Land, μg/g (ppm Wt)			1.0E-1	5.0E-2	0,02	0.01	

*To be multiplied by dilution factor

AMBIENT LEVEL GOALS					
	I. Current or Proposed Ambient Standards or Criteria		II. Toxicity Based Estimated Permissible Concentration		III. Zero Threshold Pollutants Estimated Permissible Concentration
	A. Based on Health Effects	B. Based on Ecological Effects	A. Based on Health Effects	B. Based on Ecological Effects	Based on Health Effects
Air, μg/m³ (ppm Vol)			0.5 (0.0001)		
Water, μg/l (ppm Wt)	10	5			
Land, μg/g (ppm Wt)			0.02	0.01	

CATEGORY: 78

WLN: CU

COPPER AND COPPER COMPOUNDS (AS COPPER), Cu (cuprum):

An orange, ductile, malleable metal.

STRUCTURE:

Cu Cu^{+} Cu^{+2}

PROPERTIES: Atomic number: 29; group 1b; atomic wt: 63.546; mp: 1,083 ± 0.1; bp: 2336; d: 8.92; insoluble; vap. press: 1 mm at 1628°C.

NATURAL OCCURRENCE, CHARACTERISTICS, ASSOCIATED COMPOUNDS:

Copper forms two series of compounds, cuprous (Cu^{+1}) and cupric (Cu^{+2}). Cupric compounds are the more stable. They ionize in aqueous solution.

Rural background concentration in air is reported as 0.01 to 0.41 µg/m^3 (ref. 1). Another source reports concentrations ranging from 0.06 to 0.078 as a constituent of suspended particulates in non-urban air (ref. 3). Copper salts are in the form of dusts and mists: metallic copper may occur as fume (ref. 4).

Concentration in freshwater as indicated from hydrologic benchmark samples ranges from zero to 40 µg/ℓ; out of 126 samples 87 were zero (ref. 64). Another report indicates that the average freshwater copper concentration in U. S. surface water is 13.8 µg/ℓ with a range of 0.8-280 µg/ℓ (ref. 28). Natural concentration in seawater is reported as 0.001 mg/ℓ (ref. 28) to 0.02 mg/ℓ (ref. 24). Copper imparts a taste to water in concentrations as low as 1 mg/ℓ (ref. 33). Occurrence in earth's crust is 70 ppm (ref. 24). Copper is found in soils at about 20 µg/g (ref. 126).

Copper is an essential element in plants and animals; adult intake of copper is from 2 to 4.5 mg daily (ref. 4).

TOXIC PROPERTIES, HEALTH EFFECTS:

Copper in the form of salts may cause irritation to the gastrointestinal tract if ingested; chronic exposure may result in anemia. Exposure to metallic copper fume may cause respiratory irritation, and eye and skin irritations. Damage to the liver, kidneys, and nervous system may result from exposure to copper (ref. 4,9).

LD_{50} (intraperitoneal, mouse): 3500 µg/ℓ.

LD_{50} (oral, rat): 140 mg/kg for $CuCl_2$; this is equivalent to 66 mg/kg as Cu^{+2}.

Aquatic toxicity: Copper has a synergistic action with zinc, cadmium, and mercury. Concentration of calcium and magnesium influence the toxicity of copper.

The 96 hr LC_{50} for Piephales promelas (fathead minnow) is 0.05 ppm for $CuSO_4$ in soft water, 1.4 ppm in hard water (ref. 28). Copper inhibits photosynthesis of giant kelp, at 0.06 mg/ℓ and it is toxic to oysters at 0.1 mg/ℓ (ref. 28). It has a concentration factor of 30,000 in marine phytoplankton, and 1,000 in marine fish (ref. 28).

Phytotoxicity: Copper concentrations of 0.1 to 1.0 mg/ℓ in nutrient solutions are toxic to a number of plants (ref. 28).

REGULATORY ACTIONS, STANDARDS, CRITERIA, RECOGNITION, CANDIDATE STATUS FOR SPECIFIC REGULATION:

TLV (metallic copper fume): 0.2 mg/m^3.

TLV (dusts and mists): 1 mg/m^3.

Copper is included on EPA Consent Decree Priority III List.

U.S. Public Health Service Drinking Water Regulations, 1962, Levels for Alternate Source Selection: 1.0 mg/ℓ (ref. 66).

EPA 1976 Water Quality Criteria (proposed): For domestic water supplies (welfare): 1.0 mg/ℓ; for freshwater and marine aquatic life: application factor--0.1 (to be applied to 96-hour LC_{50}, nonaerated bioassay)(ref. 33).

NAS/NAE 1972 Water Quality Criteria: For public water supply sources: 1 mg/ℓ; for freshwater aquatic life: application factor--0.1 (to be applied to 96-hour LC_{50}); for marine aquatic life: hazard level--0.05 mg/ℓ; minimal risk of deleterious effects--0.01 mg/ℓ; application factor--0.01 (to be applied to 96-hour LC_{50}); for livestock: 0.5 mg/ℓ; for irrigation: 0.20 mg/ℓ for continuous use on all soils (ref. 28).

Recommendation of U. S. Department of Agriculture and Land Grant Institutions: Copper concentration for most soils--250 kg/hectare (ref. 112).

MINIMUM ACUTE TOXICITY CONCENTRATIONS:

Air, Health: 200 µg/m^3	Air, Ecology:
Water, Health: 5 x 1000 = 5,000 µg/ℓ	Water, Health: 5 x 10 = 50 µg/ℓ
Land, Health: 0.002 x 5,000 = 10 µg/g	Land, Ecology: 0.002 x 50 = 0.1 µg/g

ESTIMATED PERMISSIBLE CONCENTRATIONS:

$EPC_{AH1} = 10^3 \times 0.2/420 = 0.5$ µg/m^3

$EPC_{WH1} = 15 \times 0.5 = 7.5$ µg/ℓ

$EPC_{WH2} = 13.8 \times 0.2 = 3$ µg/ℓ

$EPC_{WHS} = 1,000$ µg/ℓ	$EPC_{WES} = 10$ µg/ℓ
$EPC_{LH} = 0.002 \times 1000 = 2$ µg/g	$EPC_{LE} = 0.002 \times 10 = 0.2$ µg/g

MULTIMEDIA ENVIRONMENTAL GOALS

XX
78
COPPER

EMISSION LEVEL GOALS							
	I. Based on Best Technology		II. Based on Ambient Factors				
	A. Existing Standards	B. Developing Technology	A. Minimum Acute Toxicity Effluent		B. Ambient Level Goal*		C. Elimination of Discharge
	NSPS, BPT, BAT	Engineering Estimates (R&D Goals)	Based on Health Effects	Based on Ecological Effects	Based on Health Effects	Based on Ecological Effects	Natural Background*
Air, $\mu g/m^3$ (ppm Vol)			2.0E2		0.5		0.01 to 0.41
Water, $\mu g/l$ (ppm Wt)			5.0E3	5.0E1	1,000	10	13.8 1 to 20†
Land, $\mu g/g$ (ppm Wt)			1.0E1	1.0E-1	2	0.2	20

*To be multiplied by dilution factor

AMBIENT LEVEL GOALS					
	I. Current or Proposed Ambient Standards or Criteria		II. Toxicity Based Estimated Permissible Concentration		III. Zero Threshold Pollutants Estimated Permissible Concentration
	A. Based on Health Effects	B. Based on Ecological Effects	A. Based on Health Effects	B. Based on Ecological Effects	Based on Health Effects
Air, $\mu g/m^3$ (ppm Vol)			0.5		
Water, $\mu g/l$ (ppm Wt)	1,000	10			
Land, $\mu g/g$ (ppm Wt)			2	0.2	

†For seawater.

A NON-SITE-SPECIFIC TEST PLAN

Karl J. Bombaugh
Radian Corporation
Austin, Texas 78766

Abstract

An environmental assessment of a fuel conversion technology, such as Low-Btu Gasification, requires a test plan that addresses all areas of that technology. Such a plan can not be site-specific since it must be applicable to the many processes and varied operations within the technology. The plan must therefore be broad in scope. However, it must also be specific in content so that it will be applicable to the needs and problems of an actual test.

To meet this requirement, a non-site-specific test plan manual has been developed for use with low-Btu coal gasification. The manual provides basic information and procedural guidelines for the preparation and implementation of environmental assessment test plans. It defines four basic operations in test plan development. These are:

- *an engineering analysis,*
- *the definition of test purpose and test method,*
- *the selection of sampling methods, and*
- *the selection of analysis methods.*

Emphasis is placed on the development of the test method which involves defining the test's requirements and relating these requirements to the available information sources to formulate a practical test plan.

This presentation will provide a description of a non-site-specific test plan and will show how the plan can be used for a site-specific test.

INTRODUCTION

An environmental assessment of a fossil energy conversion facility should be based on valid data which accurately defines the emissions from the operation in terms of the mass and composition of the pollutants emitted. To be valid, the data used for the assessment must have been obtained under representative operating conditions by skilled technicians using reliable sampling and analytical procedures. When such data are not available in the technical literature, it must be obtained by means of an onsite test.

A program for an onsite test consists of four basic tasks involving:

- preparation,
- sampling,
- analyses, and
- data interpretation.

The preparation task is of major importance because without adequate preparation major oversites can occur which can impede the program, magnify costs, and contribute to questionable results. The preparation task should be done prior to initiating the sampling and analyses tasks.

The preparation task can be broken down into four subtasks as follows:

- defining the problem,
- reviewing the available process data,
- inspecting the plant, and
- preparing a site-specific test plan.

Major attention must be devoted to problem definition in order to avoid false starts and wasted effort.

A poorly defined problem can result in a test plan with inadequate methods, resulting in a site test that produces little useable data. Since sampling and analysis procedures are relatively problem specific they must be chosen to fit the application and to provide the level of accuracy that is required. Process data must be studied to gain an understanding of the process after which the concepts should be validated by a plant visit.

Because of the many different unit operations within a Low-Btu gasification and utilization process, the many types of processes for each operation and the many variations within any given process, a large number of site-specific test plans will be needed to assess the entire Low-Btu technology. In order to maintain a semblance of consistency in the test approach a philosophy and strategy for testing has been defined in a non-site-specific test manual. This document was developed to serve as a guide for the preparation of environmental assessment test plans for low- and medium-

Btu gasification plants. This manual does not provide the actual procedures required for a given test. It provides instead, background information and procedural guidelines which will serve as the foundation for the development and implementation of successful site-specific test plans.

This presentation will provide a description of a test plan which in this case is non-site-specific and will describe how the test plan manual is used in the preparation of a test plan for a specific site.

TEST PLAN PREPARATION

The preparation of a test plan involves operations in four areas of endeavor as follow:

- engineering analysis,
- definition of test purpose and test method,
- selection of sampling methods, and
- selection of analysis method.

The relationship between these four operations is illustrated diagramatically in Figure 1.

The engineering analysis is needed to provide information about the plant such as its physical layout and its process chemistry. This information must be reduced to a useable form. The engineering analysis includes three steps:

- review and simplify process flowsheets,
- define process modules, and
- identify streams of interest and their probable composition.

The test purpose defines the test objectives which may be any or all of the following:

- an environmental assessment,
- a control technology assessment,
- a material balance to determinetransport and fate of selected species, and
- a characterization of stream composition.

Although the purpose of the test is fixed by the information needs of a program, it has a profound effect on the detail of the test method which defines:

- the streams to be sampled,
- the species to be analyzed,
- sampling frequency,
- sampling duration,
- precision and accuracy during sampling, and
- process conditions during sampling.

The test method in turn establishes a basis for selecting methods for sampling and analysis, since the respective methods must meet the requirements set by the test method.

The sampling plan must address four major areas of activity as follows:

- preparation which includes:
    - equipment,
    - manning,
    - check-out, and
    - scheduling.
- sample collection requiring consideration of:
    - source type,
    - sample composition,
    - process conditions, and
    - information sought.
- sample preservation, and
- adaptation to deal with the unexpected.

The analysis plan must take into consideration the following:

- location - onsite or offsite analyses,
- type of samples,
- preseparations required,
- techniques of identification or quantification, and
- data validations and interpretation while on site.

The completed test plan however is not just a combination of an engineering analysis, a test method, a sampling plan, and an analysis plan. Although each of these areas of activity is distinct, they are interdependent as illustrated by the diagram in Figure 1. The decisions within each area are influenced by the test purpose and the test method which is in turn influenced by the limitations that are inherent within any or all of the involved areas.

Because of this interdependency between the respective areas, the respective plans should be prepared concurrently using corrective feedback such that the selections made for each area are made with full regard for the potential interaction with other areas. Since the scope of a site-specific test plan is defined by the test method, first attention should be devoted to its preparation. However, little can

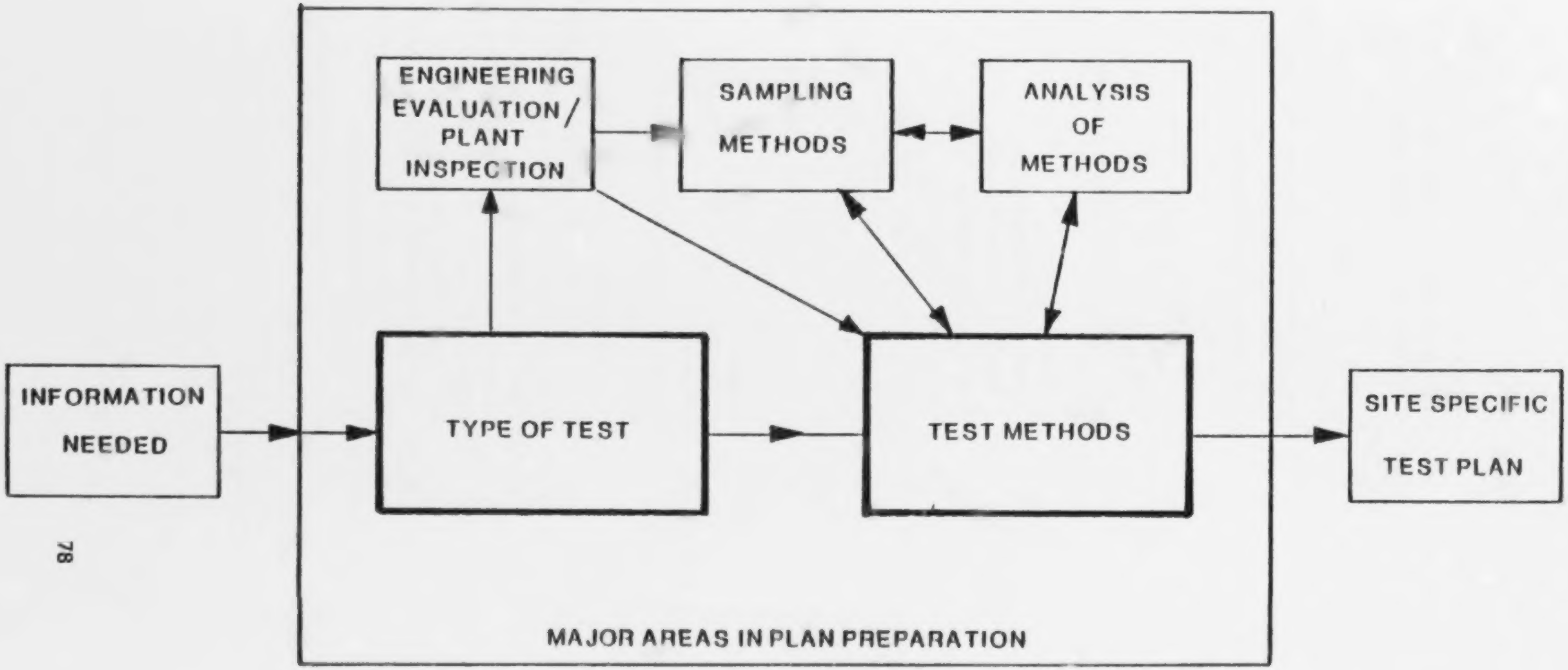

ENGINEERING EVALUATION/ PLANT INSPECTION
SAMPLING METHODS
ANALYSIS OF METHODS
INFORMATION NEEDED
TYPE OF TEST
TEST METHODS
SITE SPECIFIC TEST PLAN
MAJOR AREAS IN PLAN PREPARATION

Figure 1. Information flow diagram for the preparation of a site-specific test plan showing the interdependency of the major areas of endeavor.

be done without adequate information about the site to be tested. This information can be gained from the engineering analysis of appropriate flow sheets in the technology file using the guidelines presented in the test plan manual.

ENGINEERING ANALYSES

The engineering analysis is begun with a review of process flow sheet. If flow sheets for the specific site are not available during the initial phase of test plan development, generic diagrams of similar processes can be used until they can be replaced by authenic ones from the test site or until the generic plans can be authenticated by a site visit. In this presentation a diagram from a Lurgi plant will be used to illustrate the steps in an engineering analysis. The plans shown in Figure 2 represent a Lurgi Low-Btu coal gasification plant. In the form shown the diagram is too cumbersome to be used effectively in preparing a test plan for an environmental assessment. It should be simplified. Simplification can be accomplished by dividing the complex integrated process into unit operations and modules, e.g.

- process operations:
  coal pretreatment and handling,
  coal gasification,
  gas cleaning and purification, and
  gas utilization.
- effluent control operations:
  air pollution controls,
  water pollution controls, and
  solid waste controls.

The operation should then be subdivided into modules. For example, coal preparation can be divided into the following modules:

- drying,
- partial oxidation,
- crushing and sizing,
- pulverizing, and
- briquetting,

or the gas purification operation can be divided into:

- particulate removal,
- gas quenching, and
- acid gas removal.

Any emission control module that is associated with an operation can also be identified in this step. Detailed flow sheets for each operation of interest should be acquired in order to identify all influent and effluent streams as well as the types of emissions that are anticipated. The concept is illustrated by Figure 2. The area within the block in Figure 2 identifies the gas purification process that is expanded into a detailed flow sheet in Figure 3. The flow sheet is used to prepare a schematic diagram of the type shown in Figure 4 which identifies the types of emissions from each module. An analytical block diagram of the type shown in Figure 5 is then prepared for each module identifying each influent and effluent stream as either a process or an emission stream. (The analytical block diagram is a key tool in the engineering analyses because it provides the maximum amount of relevant information in the simplest form.) In this step the emission streams are identified and characterized as far as is possible using the data that are available.

DEFINITION OF THE TEST PURPOSE AND TEST METHOD

Test Purpose

The first and major step in the preparation of a test plan for an environmental assessment is to define the purpose of the test that may be required to obtain any or all of the following types of information about the site of interest:

- pollutant emission level,
- transport and fate of selected pollutants as they advance through the process,
- control response characteristics of operating units, and
- characterization of stream composition.

Specific requirements unique to each category, must be met by the test plan in order to obtain each type of information. (That is to say, a different type of test is needed to obtain each type of information.) For example, to determine pollutant levels one should first establish that pollutants are present. For this purpose, a comprehensive survey type of test is needed. (In such a test only minor emphasis need be placed on process conditions, sampling or analytical accuracy.) Then to obtain information on the transport and fate of a known pollutant, a more sophisticated test is needed.

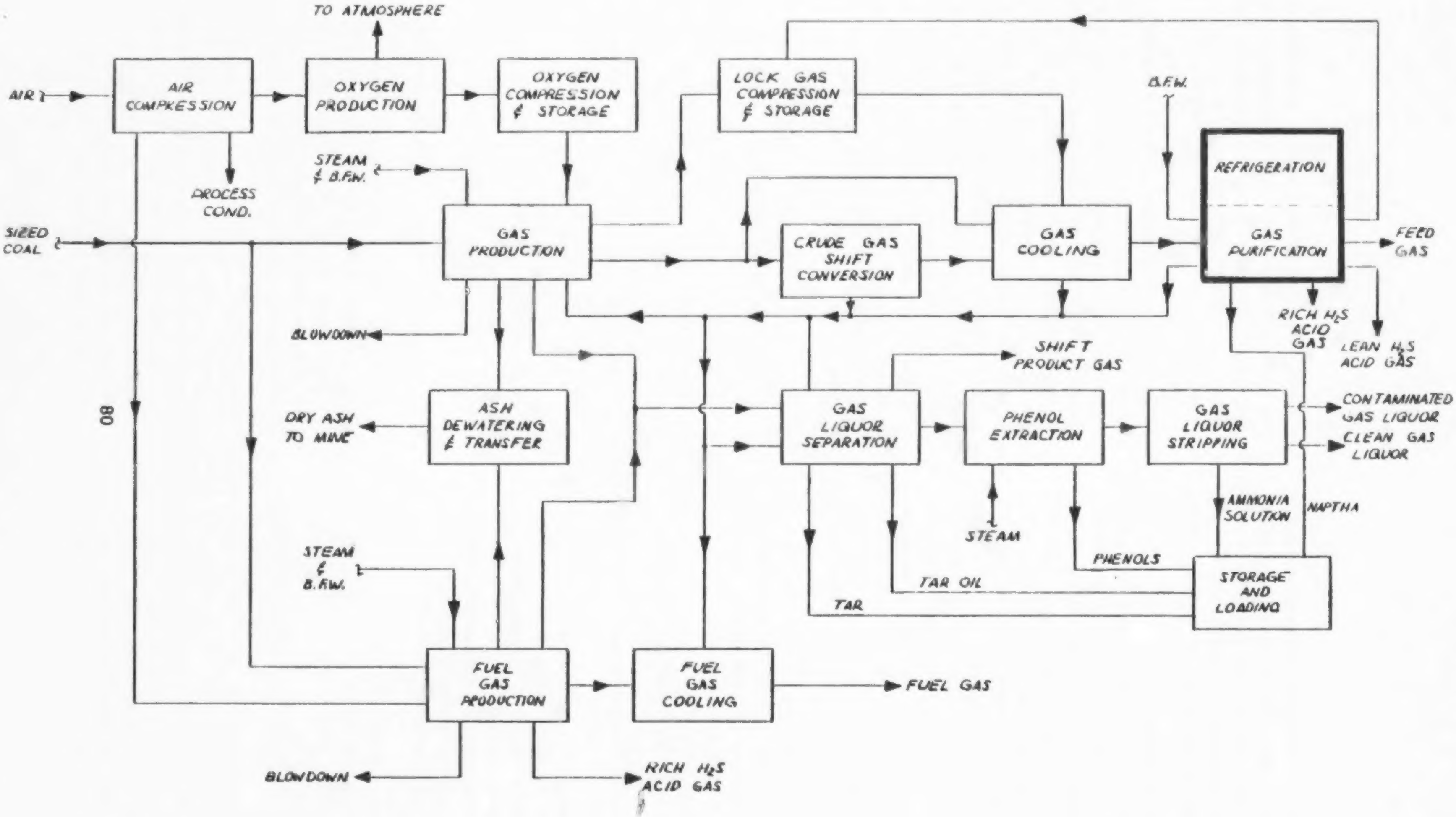

AIR
AIR COMPRESSION
PROCESS COND.
OXYGEN PRODUCTION
TO ATMOSPHERE
OXYGEN COMPRESSION & STORAGE
LOCK GAS COMPRESSION & STORAGE
B.F.W.
REFRIGERATION
GAS PURIFICATION
FEED GAS
RICH H2S ACID GAS
LEAN H2S ACID GAS
SIZED COAL
STEAM & B.F.W.
GAS PRODUCTION
CRUDE GAS SHIFT CONVERSION
GAS COOLING
BLOWDOWN
SHIFT PRODUCT GAS
DRY ASH TO MINE
ASH DEWATERING & TRANSFER
GAS LIQUOR SEPARATION
PHENOL EXTRACTION
GAS LIQUOR STRIPPING
CONTAMINATED GAS LIQUOR
CLEAN GAS LIQUOR
AMMONIA SOLUTION
NAPTHA
STEAM
PHENOLS
TAR OIL
TAR
STORAGE AND LOADING
STEAM & B.FW.
FUEL GAS PRODUCTION
FUEL GAS COOLING
FUEL GAS
BLOWDOWN
RICH H2S ACID GAS

Figure 2. Flow diagram of a coal gasification plant.

70-1101-2

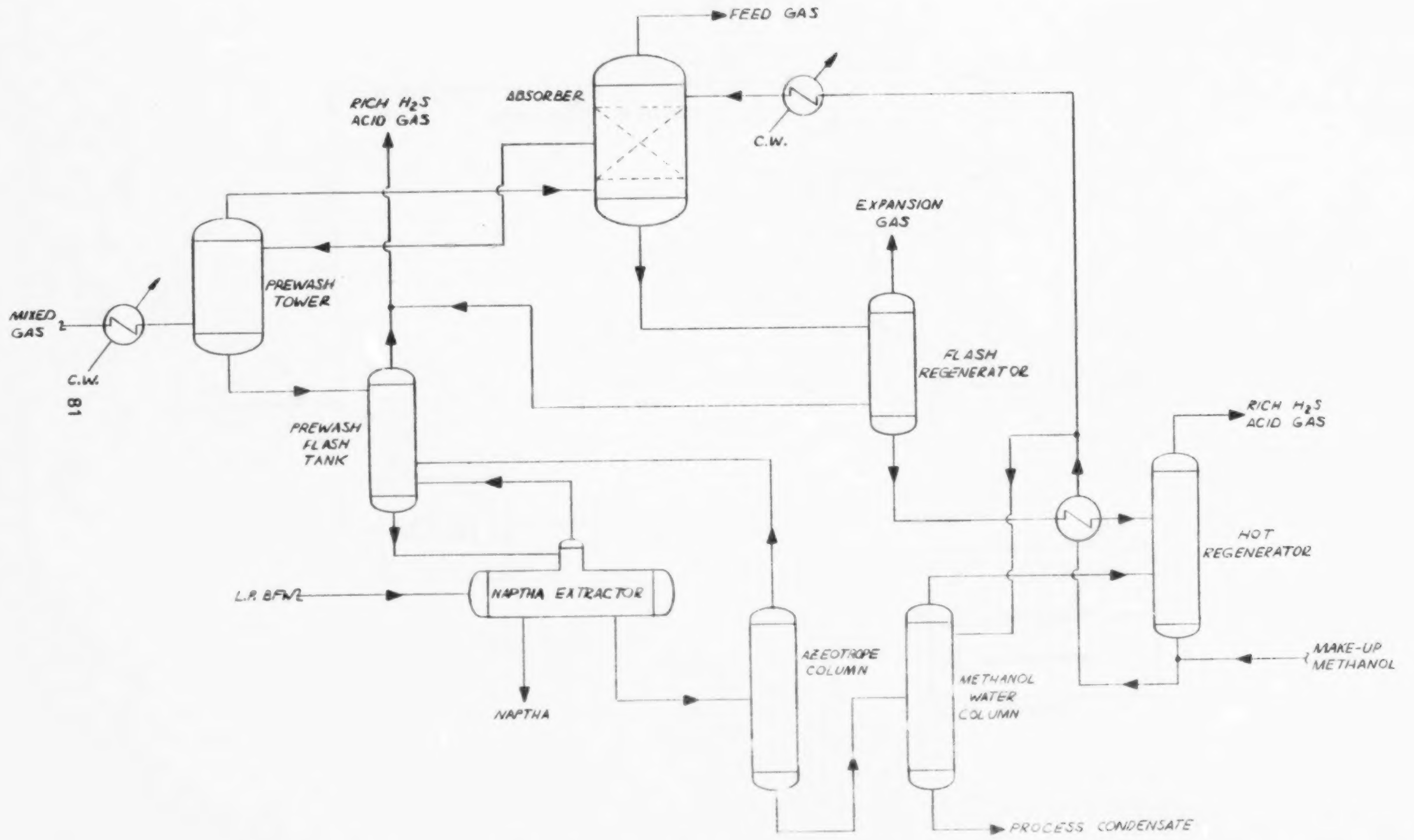

FEED GAS
ABSORBER
C.W.
RICH H_2S ACID GAS
EXPANSION GAS
MIXED GAS
PREWASH TOWER
C.W.
FLASH REGENERATOR
PREWASH FLASH TANK
RICH H_2S ACID GAS
HOT REGENERATOR
L.P. BFW
NAPTHA EXTRACTOR
AZEOTROPE COLUMN
METHANOL WATER COLUMN
MAKE-UP METHANOL
NAPTHA
PROCESS CONDENSATE

Figure 3. Gas purification and refrigeration.

70-1100-2

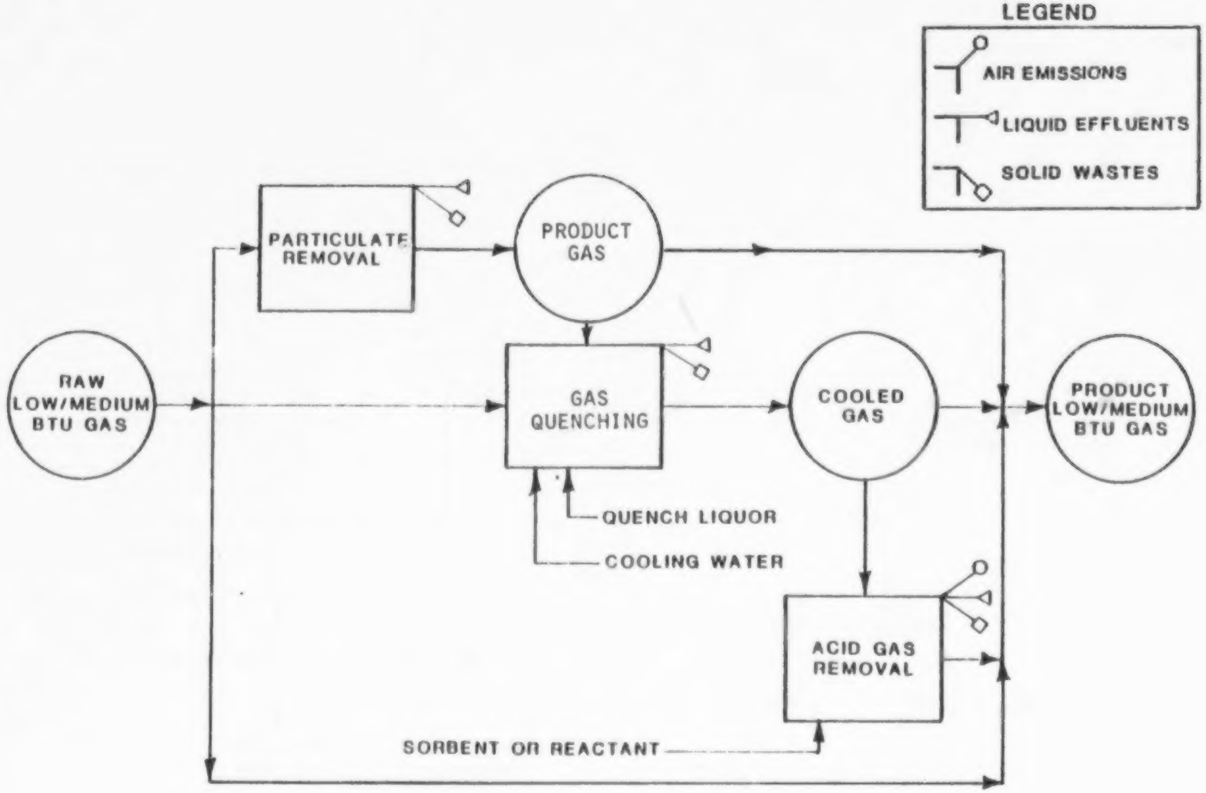

LEGEND
AIR EMISSIONS
LIQUID EFFLUENTS
SOLID WASTES
RAW LOW/MEDIUM BTU GAS
PARTICULATE REMOVAL
PRODUCT GAS
GAS QUENCHING
QUENCH LIQUOR
COOLING WATER
COOLED GAS
ACID GAS REMOVAL
SORBENT OR REACTANT
PRODUCT LOW/MEDIUM BTU GAS

Figure 4. Flow diagram for the modules in the gas purification process.

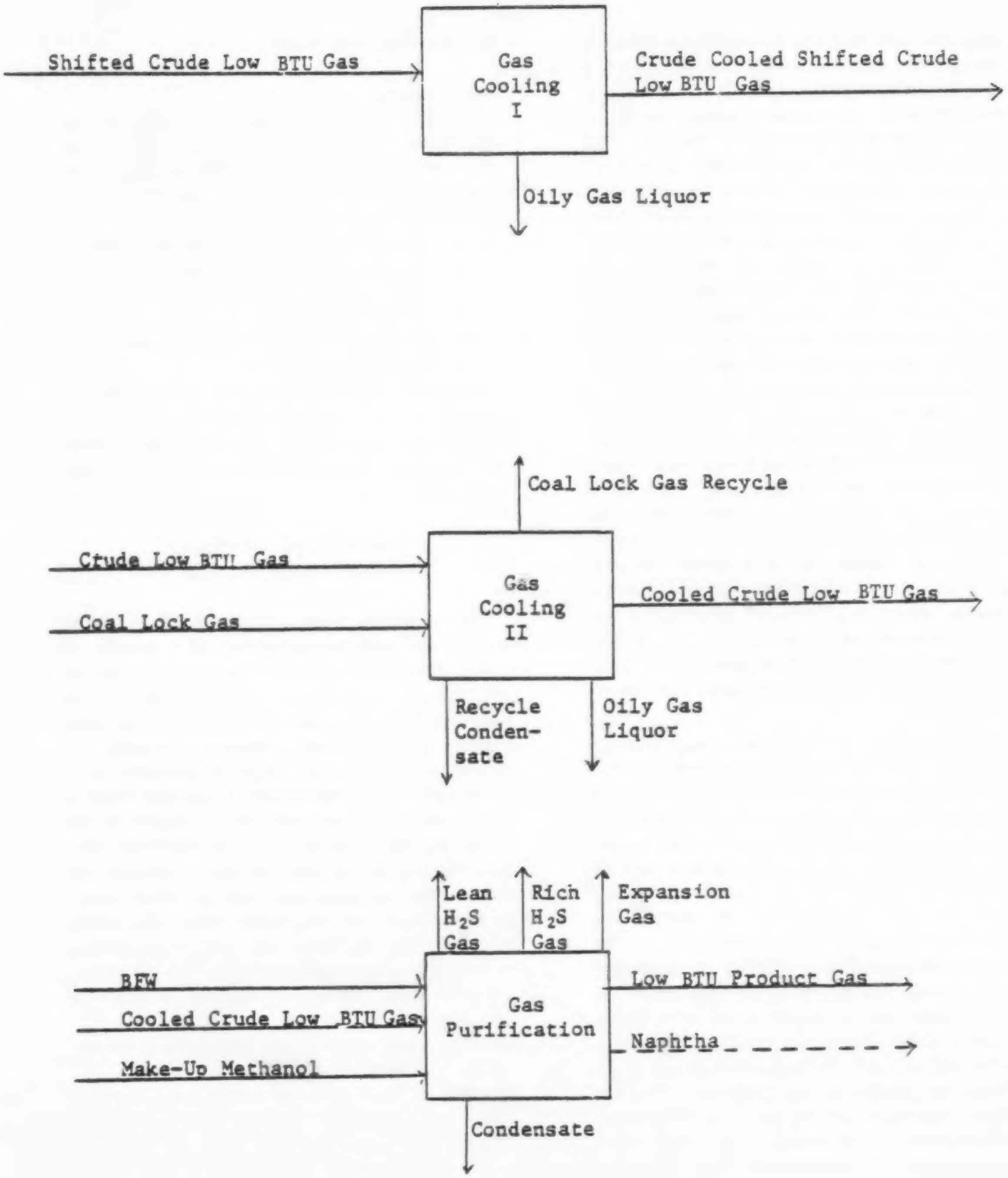

Shifted Crude Low BTU Gas
Gas Cooling I
Crude Cooled Shifted Crude Low BTU Gas
Oily Gas Liquor
Coal Lock Gas Recycle
Crude Low BTU Gas
Coal Lock Gas
Gas Cooling II
Cooled Crude Low BTU Gas
Recycle Condensate
Oily Gas Liquor
Lean H_2S Gas
Rich H_2S Gas
Expansion Gas
BFW
Cooled Crude Low BTU Gas
Make-Up Methanol
Gas Purification
Low BTU Product Gas
Naphtha
Condensate

Figure 5. Analytical modules for the gas purification operation at the El Paso Burnham complex.

This test should be made at conditions that are as near to steadystate as is feasible. Samples should be composited in order to level out the effects of minor variations. Replicate samples should be taken to increase credibility and analyses methods of high accuracy should be used so that the material balance can be closed (i.e. input = output). In contrast to either of the above, a control response test can best be done with a continuous monitor or with high frequency sampling to identify process variations. When possible the process operating conditions should be varied around the control point in order to identify trends and establish the effects of the control variables on emissions. In many cases, analysis methods providing comparatively low accuracy can be used for this application. Indeed methods of low accuracy and only acceptable reproducibility, but with rapid response, are preferred to highly accurate methods which cannot be used continuously or in real time. While an attempted material balance focuses on a fixed point in time (just as a balance sheet in a business operation), the control response test is carried out over an extended period of time and focuses on the relationship between control variables and emission response.

These concepts are illustrated diagramically in Figure 6. The concept of the control function and the balance are illustrated in Figure 6C and 6B respectively. The diagram in Figure 6A illustrates the emission level test in which attention is focused on the magnitude and type of emission without an intrinsic need for the information on the composition of either the feedstock or product. As a practical matter however, feedstock and product analyses are often included in a test program because most test programs are designed to serve a broad purpose and thereby obtain more than one type of information. Each of the various types of information is considered separately here in order to focus attention on the test's requirements which establishes its identity. Although tests for each type of information can be done separately, in practice they may be done concurrently with varying degrees of overlap. When they are integrated into a single program, care must be taken to satisfy the test requirements for each type of information sought lest the results be invalid.

Test Method

The test method defines the criteria for the test. These criteria must be met in order to obtain valid data from each of the respective information areas specified by the test's purpose. The test criteria include:

- level of accuracy and reproducibility,
- process operating conditions,
- process data requirements,
- stream selection,
- sampling frequency and duration, and
- analysis parameters.

Although the test purpose is intrinsically related to an environmental or a control technology assessment the data requirement and therefore the test criteria will vary with the data needs.

THE PHASED APPROACH OF ENVIRONMENTAL TESTING

The objective of an environmental test is to assess the pollution potential of a source. A comprehensive multimedia environmental assessment requires a comprehensive and potentially costly test program. It requires highly accurate test methods capable of characterizing a wide range of samples for a potentially broad spectrum of species from a wide variety of sources. As a means of approaching the problem in a cost effective manner, the Environmental Protection Agency has established a phased approach to environmental assessment testing which enables the tester to locate the problem area before expending costly effort to characterize it. The approach utilizes three levels of testing which are characterized as follows:

Level I: Identify problem areas using survey methods of moderate accuracy.
Level II: Characterize problem areas by identifying and accurately quantifying hazardous species in order to assess environmental burden.
Level III: Monitor selected indicator compounds to facilitate the establishment of a control technology.

This phased approach is intended to avoid the costly pitfall in an environmental assess-

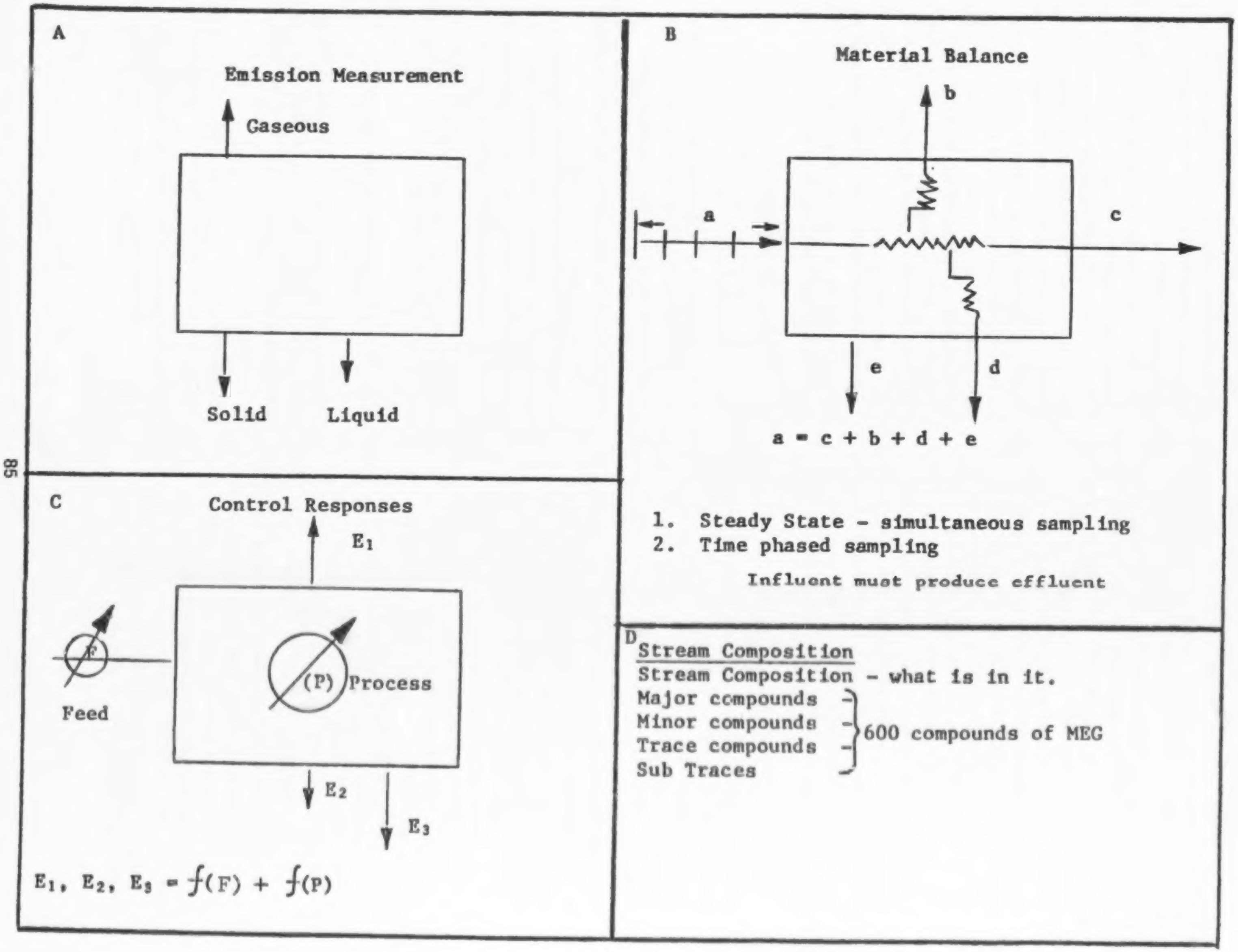

A
Emission Measurement
Gaseous
Solid
Liquid
B
Material Balance
a
b
c
d
e
a = c + b + d + e
1. Steady State - simultaneous sampling
2. Time phased sampling
Influent must produce effluent
C
Control Responses
E1
F
Feed
(P) Process
E2
E3
E1, E2, E3 = f(F) + f(P)
D
Stream Composition
Stream Composition - what is in it.
Major compounds -
Minor compounds -
Trace compounds -
Sub Traces -
600 compounds of MEG

Figure 6. Diagramatic illustration of the four types of information identifying the test's purpose.

ment test program, e. g.

- wasted effort on pollutant free emission streams or sought after pollutants that were not present,
- missed pollutants because of oversights in test planning and preparation.

The following text provides a discussion of the interrelationship between the EPA phased approach and the Non-Site-Specific Test Plan.- The Non-Site-Specific Test Plan utilizes the phased approach and uses the criteria defined by the Procedures Manual (L8501) for a Level I assessment as the basis for the initial phase. The criteria for the second and third phases of the EPA approach are at present undefined. The Non-Site-Specific Test Plan therefore provides guidelines that are based on established test procedures such that when a data need is defined and the streams of interest identified, the test specifications can be set and the respective sampling and analyses procedures chosen.

The EPA Level III test has characteristics in common with the control technology test as defined by the Non-Site-Specific Test Plan. Test methods for a control technology assessment are needed to determine the effectiveness of an emission control module.* Such a test is problem specific as well as site-specific. The Non-Site-Specific Test Plan provides a means of defining test parameters. In addition to the criteria listed previously, attention must be directed to the following factors:

- cause-effect relationships,
- process purterbations — controlled vs uncontrolled variations,
- process response time,
- interactions — dependent vs independent variables,
- process hysteresis,
- process design limitations,
- analysis response time, and
- prioritization of control variables.

The material balance is also a valuable tool for a control technology assessment since the fate of a pollutant is an integral concern with a pollution control module. At the present time use of the material balance is limited to strategic elements such as sulfur, nitrogen, and phosphorous as well as the more toxic so-called trace elements*.

Relationship Between Approaches

The three levels of the phased approach can be harmonized with the four types of information that characterize the test purpose. The relationship is shown in Table 1.

A question mark has been placed under stream composition because it is not clear whether this type of analysis will fit into the EPA strategy. An analysis of this type is highly problem specific. It can vary from a need to identify a multitude of species in a complex mixture to the need to seek out a trace of an objectionable component that interferes with the performance of an emission control module. Stream characterization can be a costly task and should be done with discretion.

Test Method Preparation

The first step in the actual preparation of the test method is to utilize the data from the engineering analysis which should enable the planner to:

- anticipate pollutants,
- identify potential fugitive emission sources,
- predict the effects of operating conditions on the flow rates and the composition of relevant streams, and
- determine if the data available is adequate to proceed to a more advanced test phase, e.g. Level II or III.

Based on the results from the engineering analysis the planner progresses with the development of the test method by defining the criteria for the test. He must bear in mind the potential restrictions that may be imposed by the sampling and analytical methods as well as by the emission source itself.

SAMPLING METHODS

Following the definition of the criteria for the test, the next major step is to develop a detailed sampling plan for the site that is to be tested.

---

*Consideration should also be given to the use of the process as a control module. See Figure 6C. Indeed a strategic control variable can exert a profound effect on the emission rate of a pollutant from a process. Several processes used in Low-Btu technology are subject to such a relationship.

TABLE 1

RELATIONSHIP BETWEEN THE TYPE OF INFORMATION SOUGHT AND THE TEST LEVEL

Type of Information	Level 1	2	3
Pollutant level	X	X	–
Fate of pollutant	–	X	–
Control response	–	–	X
Stream composition	–	?	–

The task involves specifying the locations of sampling points and selecting sampling methods. It should also include processes for sample handling.

Some considerations for sample port locations are:

- accuracy level defined by the test method,
- locations of existing ports, valves, and monitors,
- sampling practice in the test site,
- stream characteristics,
- effect of sampling on process operation, and
- safety and work area requirements.

Some considerations for sampling methods are:

- criteria defined by the test method,
- sample source,
- sample type,
- sampling techniques,
- analyses parameters, and
- external limitations.

These considerations may be expanded as follows:

- criteria defined by the test method
  - level of accuracy required,
- sample source
  - type of stream - process stream, regular or fugitive omission,
  - composition of stream,
  - temperature,
  - pressure,
  - flow,
  - type of vehicle - pipe, duct, tank, or sluice,
  - location - accessability,
  - type of port,
    - valve port,
    - hatch,
    - blind flange,
    - gas duct,
    - conveyor,
    - outflow pipe or wier,
    - open pit, sump, or pond.
- sample type
  - gas, liquid, solid or a mixture e.g.
    - gas and vapor,
    - gas and particulate,
    - liquid and solid (slurry),
  - regular or fugitive emissions.
- sampling techniques to get a representative sample
  - grab,
  - grab and composite,
  - impinger,
  - continuous monitor.
- analytical parameters
  - collection via fixation,
  - preservation - storage and transport,
  - free from contamination,
  - optimization for the analysis.
- other limitations
  - time,
  - manpower,
  - cost,
  - equipment,
  - safety,
  - plant regulations.

Provision must also be made to obtain relevant sampling data which should include the following:

- stream data
  - flow rate,
  - port location,
  - stream temperature.
- stream pressure
  - date and time of collection,
  - quantity of sample,
  - sampling method,
  - sampling handling and technique utilized for preparation,
  - sample preservation (if any).

ANALYSIS METHODS SELECTION

The final step in the preparation of the test plan is the selection of methods for the analyses. Several factors must be considered during the selection process e.g.

- the criteria fixed by the test method
  - level of accuracy,
  - species of interest,
  - type of assessment - (Level 1, 2, or 3).
- the concentration level of the species of interest,
- the presence of interfering species,
- the sampling method,
- time limitations,
- Equipment limitations, and
- cost factors.

If a Level 1 assessment is being made, the methods of analyses are specified by the Level 1 Environmental Assessment Manual (L8501). The diagram in Figure 7 outlines the approach of the Level 1 method. The diagrams in Figures 8 and 9 outline the respective approaches to inorganic and the organic analyses. These methods are still in a state of evaluation and are subject to modification. The methods for Level 2 analyses have not yet been specified. However, as greater specificity and accuracy is required, methods must be selected that are capable of meeting the higher requirements. In place of spark source mass spectrometry, which is an ideal survey tool for trace elements, a combination of techniques may be required. The diagram in Figure 10 shows an approach that can be used to determine 31 different elements on samples such as those obtained from a Low-Btu gasification process.

The approach to the determination of individual species of organic compounds is even more complex than that for inorganic species. A worthy objective is to preseparate the samples into acidic, basic, and neutral fractions for subsequent analyses of "volatile and semivolatile" species by GC-MS. This approach provides access to the extensive computerized data banks that are commercially available. Nonvolatile substances of interest can be further characterized by auxilliary techniques. Following separation by High Performance Liquid Chromatography, fractions can be characterized by IR, FTIR, NMR, and UV and fluorescence spectrometry or such other techniques as are justified.

This approach, outlined in Figures 11 and 12, is completely modular and separates the sample into 9 fractions, seven of which (with the exception of macromolecules) can be characterized to a large extent by GC-MS.

Whether the approach be to characterize a sample in order to determine "what it contains" or to analyze it for specified environmentally hazardous species, the modular scheme provides a most versatile approach that can be adapted to a wide range of conditions.

SUMMARY

The Non-site-specific Test Plan provides a systematic approach to environmental test preparation. This approach makes it possible to anticipate many of the problems that would be encountered at a test site. It also makes it possible to give prior considerations to the potential solutions to these problems. A manual has been developed that provides guidelines for these considerations.

REFERENCES

1. James M. Harless and Karl J. Bombaugh. *A Non-site Specific Test Plan Manual for the Characterization of Low/Medium-Btu Gasification Facilities.* EPA Contract No. 68-02-2147. Radian Project No. 200-143-10. Radian Corporation, Austin, Texas, July 1977.
2. J. H. Hamersma, S. F. Reynolds, and R. F. Maddalene, IERL-RTP Procedures Manual: Level 1 Environmental Assessment. Report No. EPA 600/2-76-160A. EPA Contract No. 68-02-1412, Task 18, Redondo Beach, Ca. TRW Systems Group, June 1976.

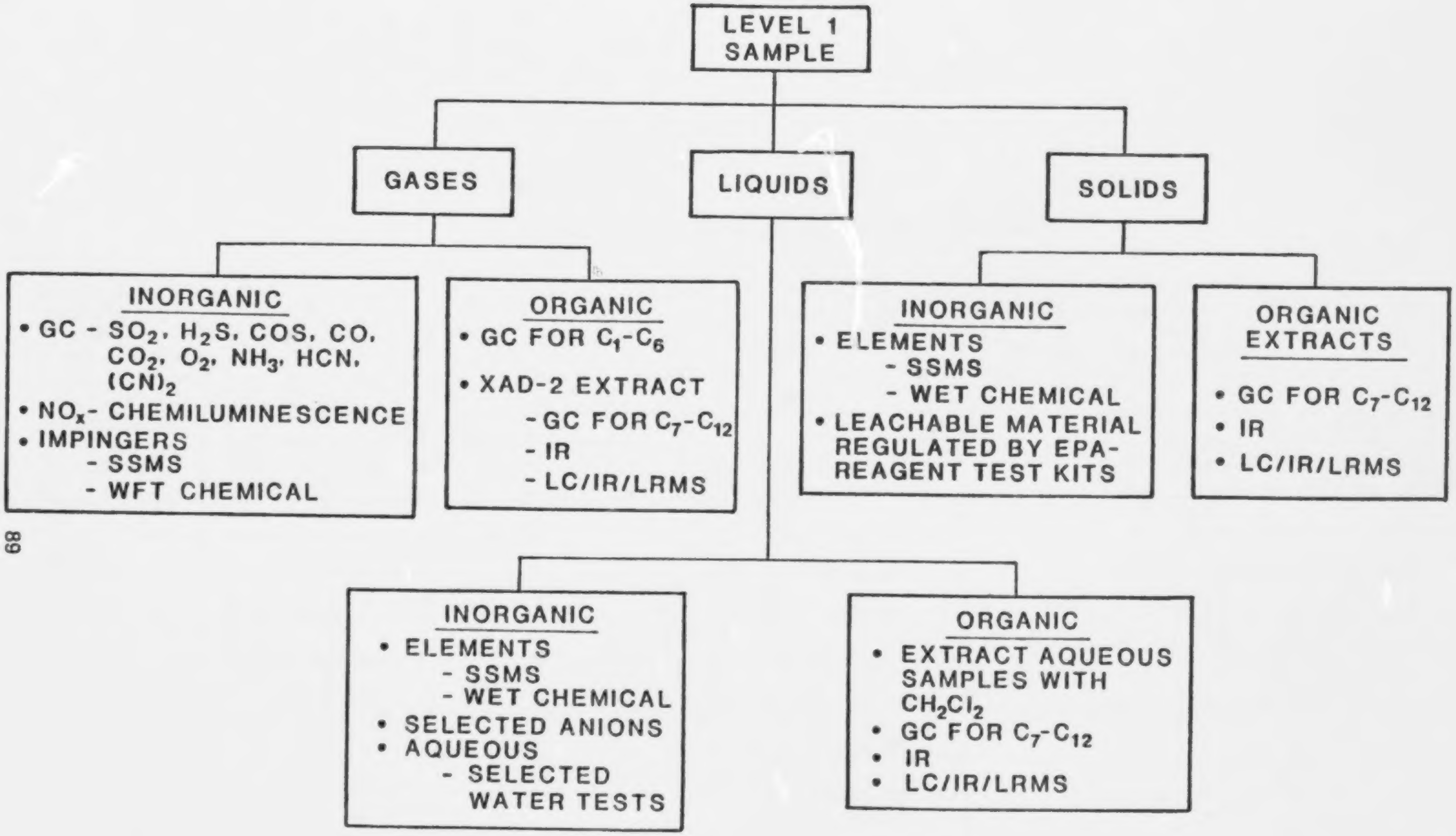

LEVEL 1 SAMPLE
GASES
LIQUIDS
SOLIDS
INORGANIC
• GC - SO_2, H_2S, COS, CO, CO_2, O_2, NH_3, HCN, $(CN)_2$
• NO_x- CHEMILUMINESCENCE
• IMPINGERS
- SSMS
- WFT CHEMICAL
ORGANIC
• GC FOR C_1-C_6
• XAD-2 EXTRACT
- GC FOR C_7-C_{12}
- IR
- LC/IR/LRMS
INORGANIC
• ELEMENTS
- SSMS
- WET CHEMICAL
• LEACHABLE MATERIAL REGULATED BY EPA-REAGENT TEST KITS
ORGANIC EXTRACTS
• GC FOR C_7-C_{12}
• IR
• LC/IR/LRMS
INORGANIC
• ELEMENTS
- SSMS
- WET CHEMICAL
• SELECTED ANIONS
• AQUEOUS
- SELECTED WATER TESTS
ORGANIC
• EXTRACT AQUEOUS SAMPLES WITH CH_2Cl_2
• GC FOR C_7-C_{12}
• IR
• LC/IR/LRMS

Figure 7. Outline of Level 1 analysis.

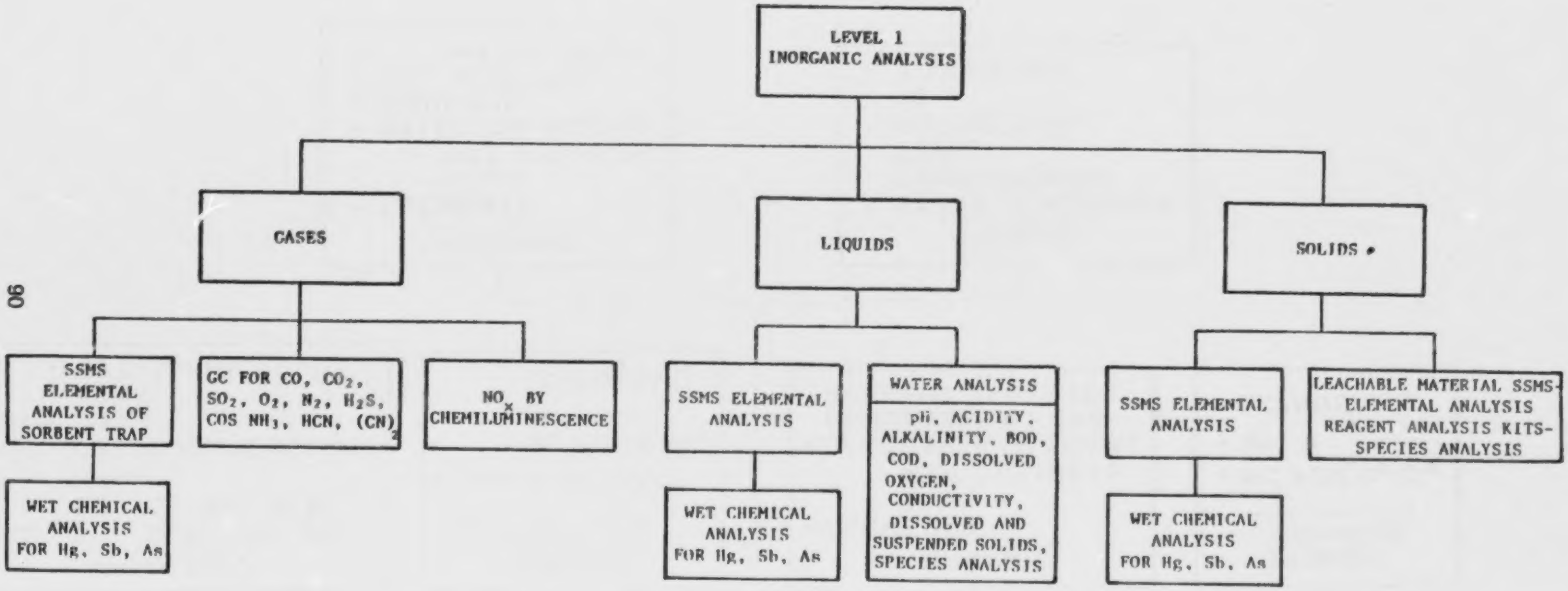

LEVEL 1
INORGANIC ANALYSIS
GASES
LIQUIDS
SOLIDS *
SSMS ELEMENTAL ANALYSIS OF SORBENT TRAP
GC FOR CO, CO₂, SO₂, O₂, N₂, H₂S, COS NH₃, HCN, (CN)₂
NOx BY CHEMILUMINESCENCE
WET CHEMICAL ANALYSIS FOR Hg, Sb, As
SSMS ELEMENTAL ANALYSIS
WATER ANALYSIS
pH, ACIDITY, ALKALINITY, BOD, COD, DISSOLVED OXYGEN, CONDUCTIVITY, DISSOLVED AND SUSPENDED SOLIDS, SPECIES ANALYSIS
WET CHEMICAL ANALYSIS FOR Hg, Sb, As
SSMS ELEMENTAL ANALYSIS
LEACHABLE MATERIAL SSMS-ELEMENTAL ANALYSIS REAGENT ANALYSIS KITS-SPECIES ANALYSIS
WET CHEMICAL ANALYSIS FOR Hg, Sb, As

Figure 8. Outline of Level 1 inorganic analysis.

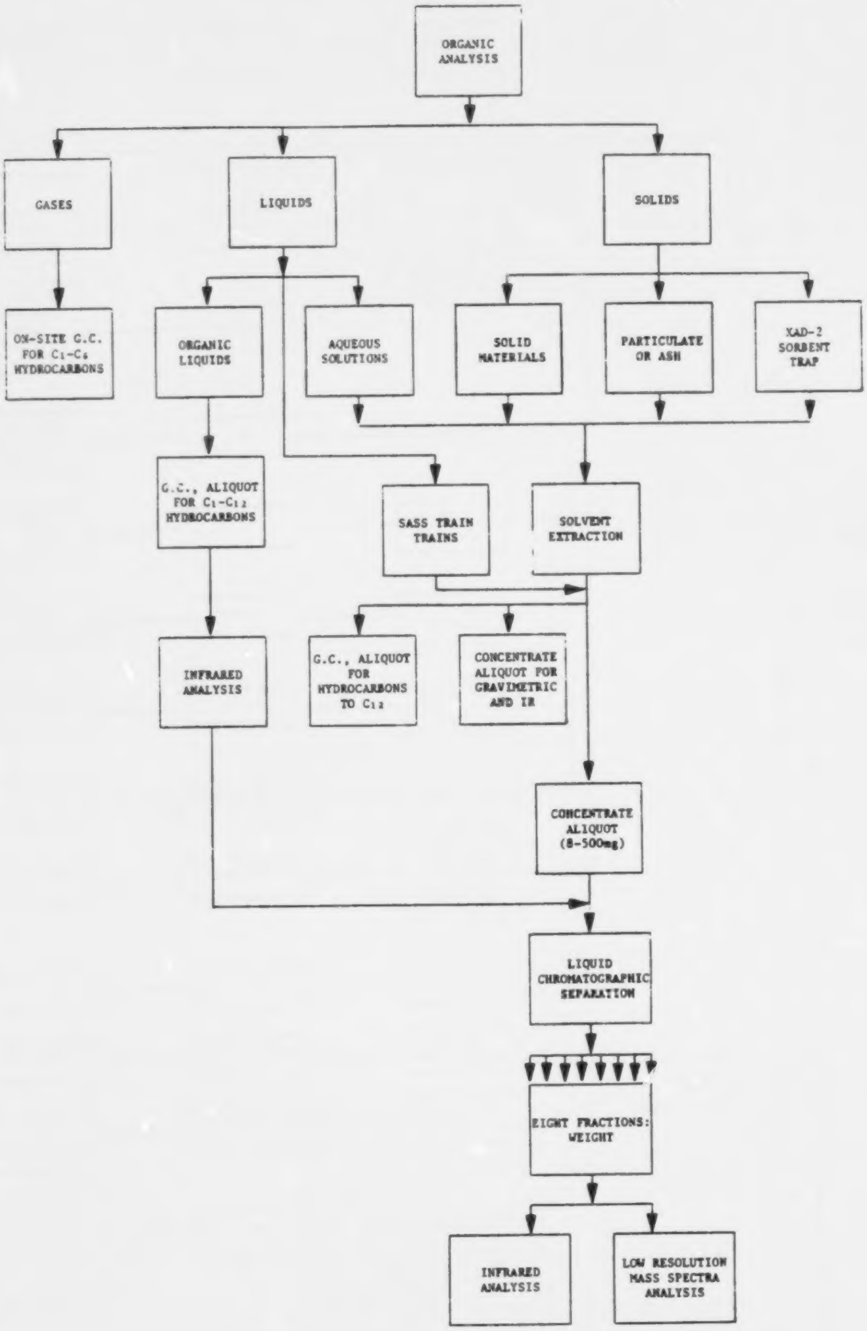

ORGANIC ANALYSIS
GASES
LIQUIDS
SOLIDS
ON-SITE G.C. FOR C1-C6 HYDROCARBONS
ORGANIC LIQUIDS
AQUEOUS SOLUTIONS
SOLID MATERIALS
PARTICULATE OR ASH
XAD-2 SORBENT TRAP
G.C., ALIQUOT FOR C1-C12 HYDROCARBONS
SASS TRAIN TRAINS
SOLVENT EXTRACTION
INFRARED ANALYSIS
G.C., ALIQUOT FOR HYDROCARBONS TO C12
CONCENTRATE ALIQUOT FOR GRAVIMETRIC AND IR
CONCENTRATE ALIQUOT (8-500mg)
LIQUID CHROMATOGRAPHIC SEPARATION
EIGHT FRACTIONS: WEIGHT
INFRARED ANALYSIS
LOW RESOLUTION MASS SPECTRA ANALYSIS

Figure 9. Outline of level 1 organic analyses.

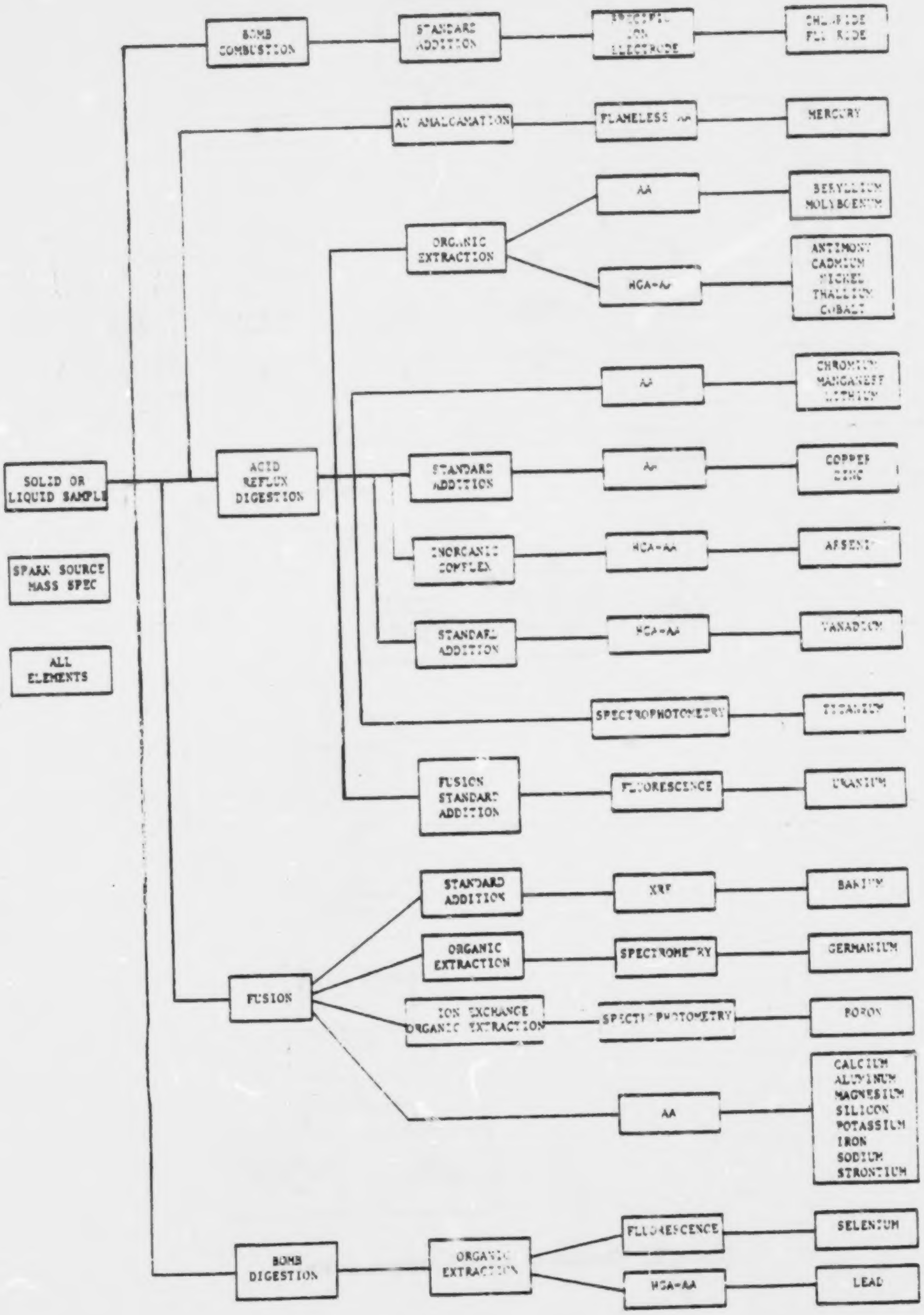

SOLID OR LIQUID SAMPLE
SPARK SOURCE MASS SPEC
ALL ELEMENTS
BOMB COMBUSTION
STANDARD ADDITION
SPECIFIC ION ELECTRODE
CHLORIDE FLUORIDE
AU AMALGAMATION
FLAMELESS AA
MERCURY
ACID REFLUX DIGESTION
ORGANIC EXTRACTION
AA
BERYLLIUM MOLYBDENUM
HGA-AA
ANTIMONY CADMIUM NICKEL THALLIUM COBALT
AA
CHROMIUM MANGANESE LITHIUM
STANDARD ADDITION
AA
COPPER ZINC
INORGANIC COMPLEX
HGA-AA
ARSENIC
STANDARD ADDITION
HGA-AA
VANADIUM
SPECTROPHOTOMETRY
TITANIUM
FUSION STANDARD ADDITION
FLUORESCENCE
URANIUM
FUSION
STANDARD ADDITION
XRF
BARIUM
ORGANIC EXTRACTION
SPECTROMETRY
GERMANIUM
ION EXCHANGE ORGANIC EXTRACTION
SPECTROPHOTOMETRY
BORON
AA
CALCIUM ALUMINUM MAGNESIUM SILICON POTASSIUM IRON SODIUM STRONTIUM
BOMB DIGESTION
ORGANIC EXTRACTION
FLUORESCENCE
SELENIUM
HGA-AA
LEAD

Figure 10. Analysis of inorganic elements.

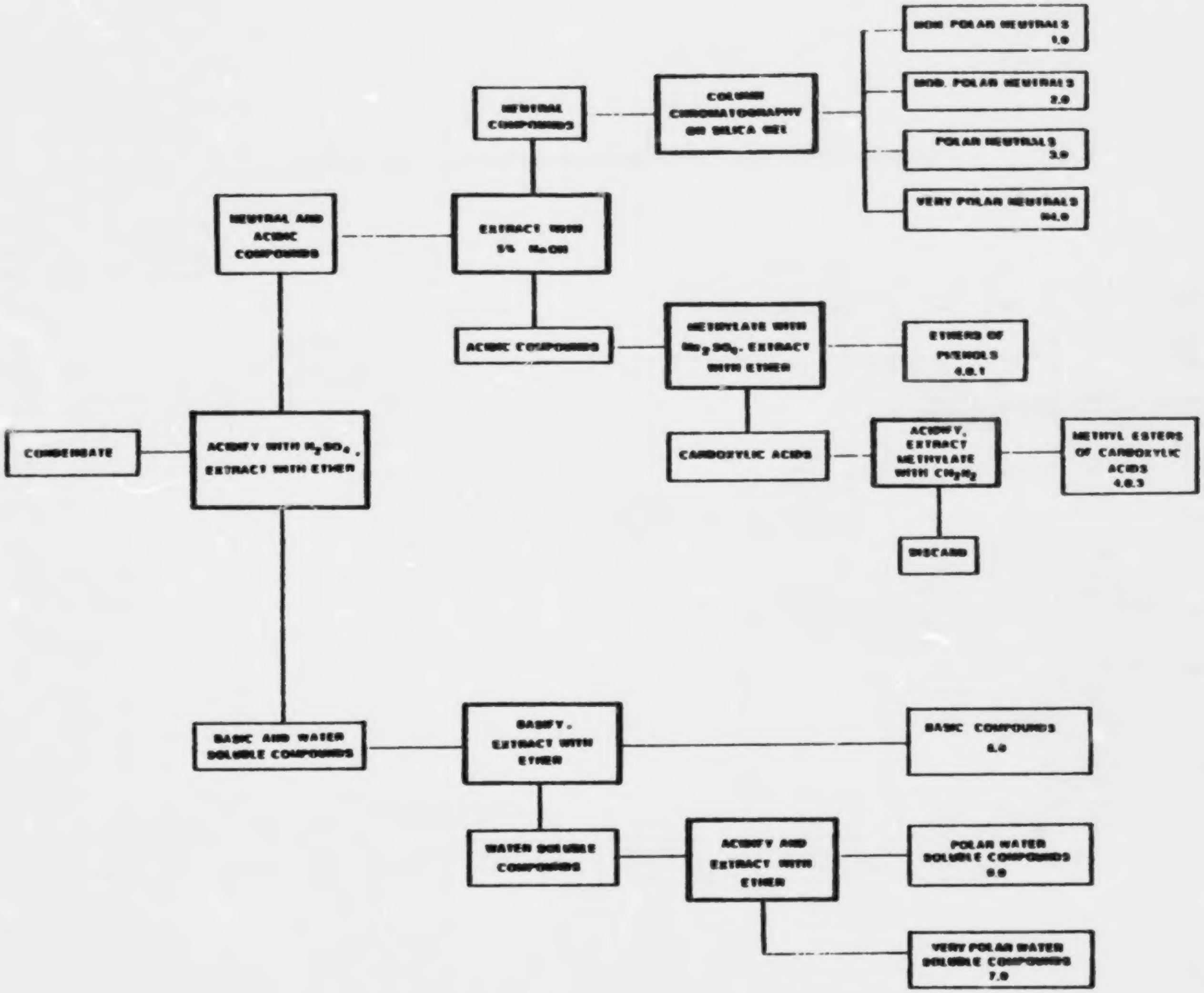

CONDENSATE
ACIDIFY WITH H_2SO_4, EXTRACT WITH ETHER
NEUTRAL AND ACIDIC COMPOUNDS
EXTRACT WITH 5% NaOH
NEUTRAL COMPOUNDS
COLUMN CHROMATOGRAPHY ON SILICA GEL
NON POLAR NEUTRALS 1.0
MOD. POLAR NEUTRALS 2.0
POLAR NEUTRALS 3.0
VERY POLAR NEUTRALS 3A.0
ACIDIC COMPOUNDS
METHYLATE WITH Me_2SO_4, EXTRACT WITH ETHER
ETHERS OF PHENOLS 4.0.1
CARBOXYLIC ACIDS
ACIDIFY, EXTRACT METHYLATE WITH CH_2N_2
METHYL ESTERS OF CARBOXYLIC ACIDS 4.0.3
DISCARD
BASIC AND WATER SOLUBLE COMPOUNDS
BASIFY, EXTRACT WITH ETHER
BASIC COMPOUNDS 5.0
WATER SOLUBLE COMPOUNDS
ACIDIFY AND EXTRACT WITH ETHER
POLAR WATER SOLUBLE COMPOUNDS 6.0
VERY POLAR WATER SOLUBLE COMPOUNDS 7.0

Figure 11. Separation of trace organic species.

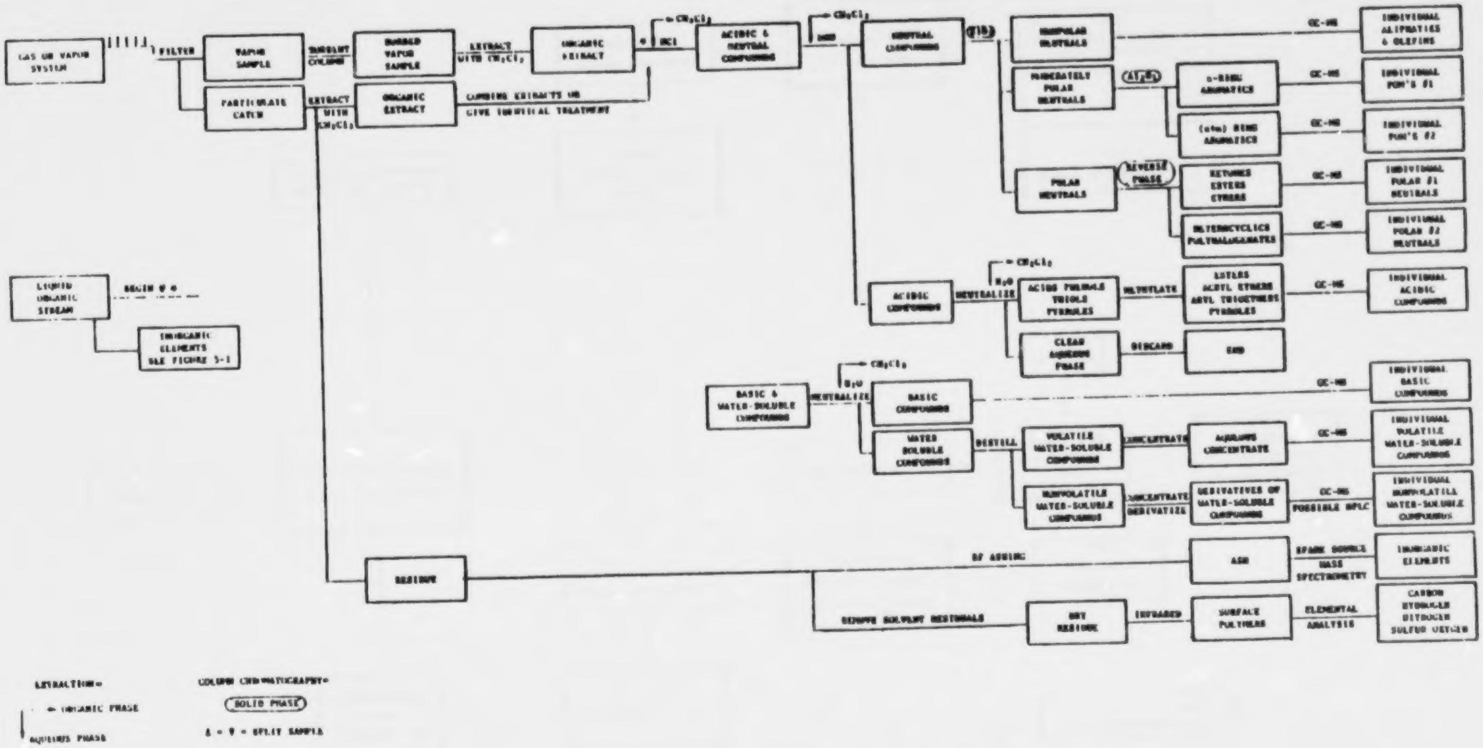

GAS OR VAPOR SYSTEM
FILTER
VAPOR SAMPLE
PARTICULATE CATCH
SORBENT COLUMN
SORBED VAPOR SAMPLE
EXTRACT WITH CH_2Cl_2
ORGANIC EXTRACT
EXTRACT WITH CH_2Cl_2
ORGANIC EXTRACT
COMBINE EXTRACTS OR GIVE IDENTICAL TREATMENT
HCl
CH_2Cl_2
ACIDIC & NEUTRAL COMPOUNDS
NaOH
CH_2Cl_2
NEUTRAL COMPOUNDS
TLC
NONPOLAR NEUTRALS
GC-MS
INDIVIDUAL ALIPHATICS & OLEFINS
MODERATELY POLAR NEUTRALS
Al_2O_3
n-RING AROMATICS
GC-MS
INDIVIDUAL PAH'S #1
(n+m) RING AROMATICS
GC-MS
INDIVIDUAL PAH'S #2
POLAR NEUTRALS
REVERSE PHASE
KETONES ESTERS ETHERS
GC-MS
INDIVIDUAL POLAR #1 NEUTRALS
HETEROCYCLICS POLYHALOGENATES
GC-MS
INDIVIDUAL POLAR #2 NEUTRALS
ACIDIC COMPOUNDS
NEUTRALIZE
H_2O
CH_2Cl_2
ACIDS PHENOLS THIOLS PYRROLES
METHYLATE
ESTERS ACETYL ETHERS ARYL THIOETHERS PYRROLES
GC-MS
INDIVIDUAL ACIDIC COMPOUNDS
CLEAR AQUEOUS PHASE
DISCARD
END
LIQUID ORGANIC STREAM
BEGIN @ ⊕
INORGANIC ELEMENTS SEE FIGURE 5-1
BASIC & WATER-SOLUBLE COMPOUNDS
NEUTRALIZE
H_2O
CH_2Cl_2
BASIC COMPOUNDS
GC-MS
INDIVIDUAL BASIC COMPOUNDS
WATER SOLUBLE COMPOUNDS
DISTILL
VOLATILE WATER-SOLUBLE COMPOUNDS
CONCENTRATE
AQUEOUS CONCENTRATE
GC-MS
INDIVIDUAL VOLATILE WATER-SOLUBLE COMPOUNDS
NONVOLATILE WATER-SOLUBLE COMPOUNDS
CONCENTRATE DERIVATIZE
DERIVATIVES OF WATER-SOLUBLE COMPOUNDS
GC-MS POSSIBLE HPLC
INDIVIDUAL NONVOLATILE WATER-SOLUBLE COMPOUNDS
RESIDUE
BY ASHING
ASH
SPARK SOURCE MASS SPECTROMETRY
INORGANIC ELEMENTS
REMOVE SOLVENT RESIDUALS
DRY RESIDUE
INFRARED
SURFACE POLYMERS
ELEMENTAL ANALYSIS
CARBON HYDROGEN NITROGEN SULFUR OXYGEN
EXTRACTION=
← ORGANIC PHASE
AQUEOUS PHASE
COLUMN CHROMATOGRAPHY=
SOLID PHASE
Δ = ∇ = SPLIT SAMPLE

Figure 12. Separation and analysis of trace organic species.

ORGANIC ANALYSIS FOR ENVIRONMENTAL ASSESSMENT

L. D. Johnson
R. G. Merrill

Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

September 1977

Abstract

A survey analysis approach for organic materials is presented. The scheme presented is relatively simple and inexpensive, yet produces useful information which can be utilized to decide whether more sophisticated and expensive methods are justified. A selection of Level 1 data from environmental samples is presented.

A brief discussion of Level 2 analysis techniques is also included.

INTRODUCTION

Two of the major responsibilities of EPA's Industrial Environmental Research Laboratory in North Carolina (IERL/RTP) are control technology development and environmental assessment. Due to a growing awareness and concern over the effect of pollution in our surroundings, the current emphasis is on environmental assessment.

Worldwide energy shortages have added momentum to development programs for alternate or modified energy or fuels production. It is particularly important that these emerging technologies be evaluated, as they develop, for their potential environmental insult. By means of such early investigation, problem processes may be modified at the most effective and economical stage, or control technology may be developed in parallel with production technology.

Only a few existing industrial processes have been reasonably well characterized with respect to their release of a few selected pollutants. Far fewer, if indeed any, processes have been adequately studied for a wide range of potentially harmful materials. For this reason, control technology needs will remain undefined until the potential environmental effects are estimated.

Environmental assessment is a formidable task, technically difficult, and extremely expensive. In order to help maximize the information gain of such programs and to minimize the costs, special approaches have been developed to sampling and analysis programs for environmental assessment. This paper discusses one part of such an approach: organic analysis employed in Level 1 of an environmental assessment.

FUNDAMENTALS

Before discussing the organic analysis approach employed in Level 1 of an environmental assessment, it is appropriate to consider some of the pertinent terminology. To say that an environmental assessment is a project involving problem definition with regard to pollutant source environmental insult is convenient, but perhaps an oversimplification. A longer, but more complete, description is that an IERL/RTP environmental assessment contains: (1) a systematic evaluation of the physical, chemical, and biological characteristics of all streams associated with a process; (2) predictions of the probable effects of those streams on the environment; (3) prioritization of those streams relative to their individual hazard potential; and (4) identification of any necessary control technology programs.

Examination of several strategies for environmental assessment sampling and analysis led to the conclusion that a phased approach was the most cost and information effective. The phased approach has been discussed in several recent publications (1, 2, 3, 4). This strategy makes use of three levels of sampling and analysis: Level 1 is a survey phase; Level 2 is a directed detailed analysis, based on Level 1 information; and Level 3 involves monitoring of priority pollutants selected by use of information generated during the two previous phases. Level 1 sampling and sample preparation procedures are dealt with in several publications (5, 6, 7, 8). A flow chart of the Level 1 analysis scheme, shown in Figure 1, contains four major divisions of analysis: physical, inorganic chemical, organic chemical, and biological. Organic analysis will be the primary topic discussed from this point on.

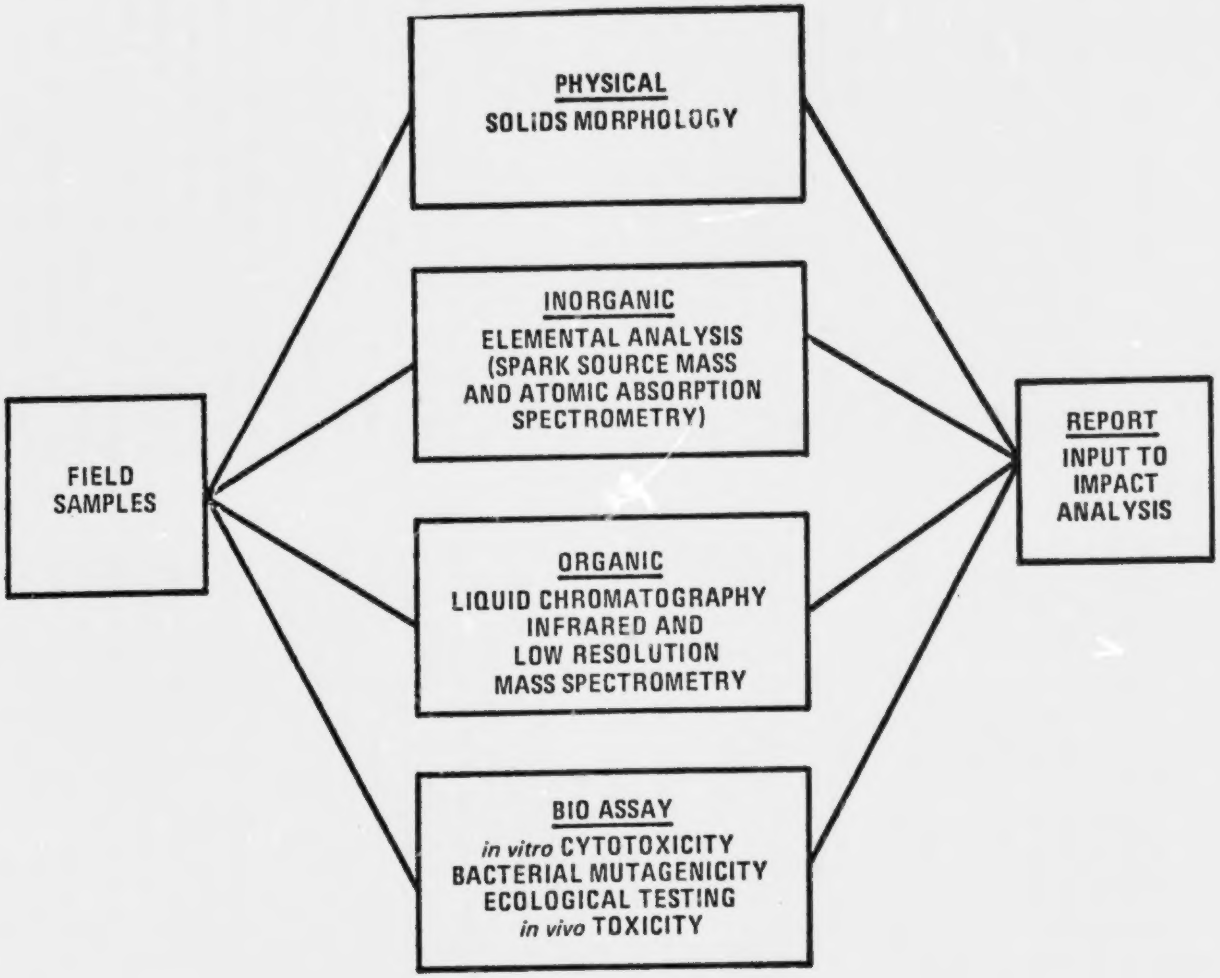

FIELD SAMPLES
PHYSICAL
SOLIDS MORPHOLOGY
INORGANIC
ELEMENTAL ANALYSIS (SPARK SOURCE MASS AND ATOMIC ABSORPTION SPECTROMETRY)
ORGANIC
LIQUID CHROMATOGRAPHY INFRARED AND LOW RESOLUTION MASS SPECTROMETRY
BIO ASSAY
in vitro CYTOTOXICITY
BACTERIAL MUTAGENICITY
ECOLOGICAL TESTING
in vivo TOXICITY
REPORT
INPUT TO IMPACT ANALYSIS

Figure 1. Flow chart of level 1 scheme.

ORGANIC ANALYSIS OVERVIEW

Current analytical technology makes it possible to identify and quantify virtually all of the organic constituents of even the most complex mixture, given sufficient sample, funds, and time. Obviously all three will not be available for every case; hence, adjustments must be made in the degree of information expected from the sample. Specific compound identification should not, in general, be expected at costs commensurate with the Level 1 philosophy. Therefore, the scheme presented is relatively simple and inexpensive, yet produces information which can be utilized to decide whether more sophisticated and expensive methods are justified. The Level 1 organic analysis produces data in terms of chromatographic classes of compounds and characteristic infrared absorption bands. The Level 1 organic analysis strategy shown in Figure 2 shows four analytical operations that are central to the scheme.

Liquid chromatographic separation (Appendix A.1) is the heart of the whole approach. It is an analytical step (in that behavior of a given class of compounds is predictable) as well as a separation step (since the fractions may be further analyzed much more readily than the original mixture). The behavior of selected classes of compounds with respect to the chromatographic analysis is shown in Figure 3. Distribution of a few selected compounds is shown in Figure 4.

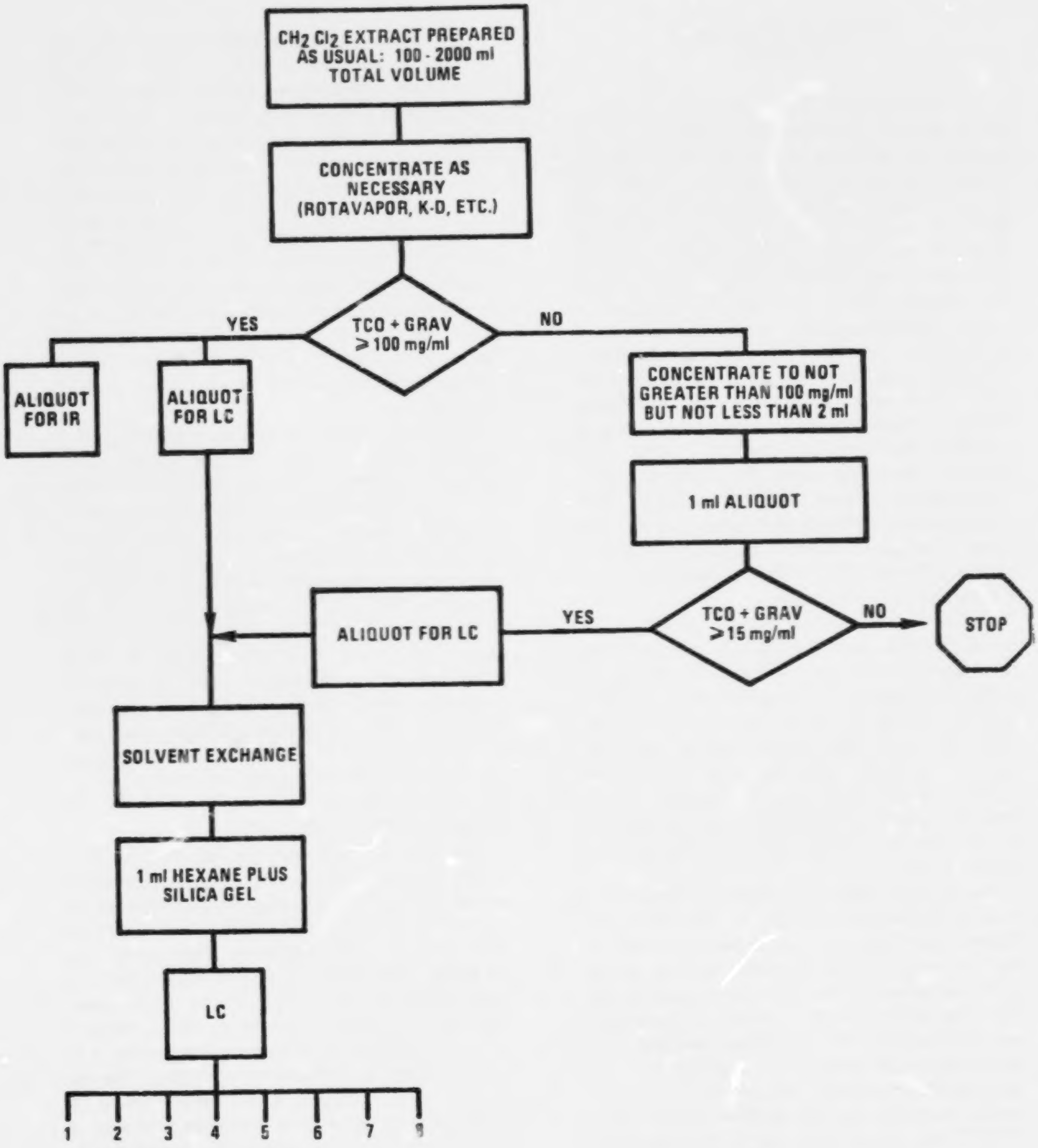
The second analysis operation is determination of total organics content. This operation allows quantitation of the organics in each of the chromatographic fractions as well as aliquot size selection for optimum column operation. The original Level 1 scheme (8), as well as the first revision (5), depended entirely upon reduction to dryness and weighing for total organics determination. Recent data show that many materials in the boiling range below 275°C may be partially lost by that approach (9). Accordingly, a gas chromatography procedure for volatile organics has been adopted as a part of the Level 1 strategy (Appendix A.2). Total organic content is obtained by addition of the gravimetric results and the total chromatographable organics (TCO).

The third analysis operation is infrared absorption spectrophotometry. This classical technique is often overlooked in today's mass-spectrometry-dominated laboratory, but still remains a powerful tool which provides considerable information at moderate cost. Infrared spectra of the eight chromatographic fractions may be used to confirm the absence or presence of particular compound classes or functional groups as indicated by the chromatograhic data. It is occasionally possible to obtain specific compound identification from the infrared spectra; but as previously mentioned, the complexity of most environmental samples makes this the exception rather than the rule.

The fourth analytical operation of the Level 1 organic scheme is low resolution mass spectrometry (LMRS). This particular tool, sitting firmly in the middle of the transition zone between Levels 1 and 2, causes many philosophical problems concerning its proper utilization. The original Level 1 scheme did not contain LRMS (8); but, it was included in the modified strategy (5) to prevent potential triggering of Level 2 efforts based on large amounts of suspicious, but innocuous, organics. LRMS can be a very powerful tool, especially when combined with the other Level 1 components. In many cases, compound identification and quantification are possible when the entire scheme is applied. What, then, are the philosophical problems?

The first and foremost problem is cost. One LRMS application including interpretation costs about $100, not a large sum compared to overall Level 1 costs. If LRMS is necessary on only one or two fractions, then costs are nominal, information gain is considerable, and cost effectiveness is high. In the worst case, however, one may be forced to apply LRMS to all eight fractions and employ both probe and batch modes of sample introduction. The resultant LRMS cost is $1600 per sample, a significant increase. The cost impact of such a per-sample increase may be forcefully illustrated by the following hypothetical example.

If three flue gas samples are taken with a Source Assessment Sampling System (SASS) at each of 50 plants, the resulting number of subsamples requiring Level 1 organic analysis


CH2 Cl2 EXTRACT PREPARED AS USUAL: 100 - 2000 ml TOTAL VOLUME
CONCENTRATE AS NECESSARY (ROTAVAPOR, K-D, ETC.)
YES
TCO + GRAV ⩾ 100 mg/ml
NO
ALIQUOT FOR IR
ALIQUOT FOR LC
CONCENTRATE TO NOT GREATER THAN 100 mg/ml BUT NOT LESS THAN 2 ml
1 ml ALIQUOT
ALIQUOT FOR LC
YES
TCO + GRAV ⩾ 15 mg/ml
NO
STOP
SOLVENT EXCHANGE
1 ml HEXANE PLUS SILICA GEL
LC
1
2
3
4
5
6
7
8

EACH FRACTION: TCO + GRAV
IR ON GRAV SAMPLE
LRMS BY BATCH AND PROBE. (OPTIONAL)

Figure 2. Modified level 1 organic analysis procedure.

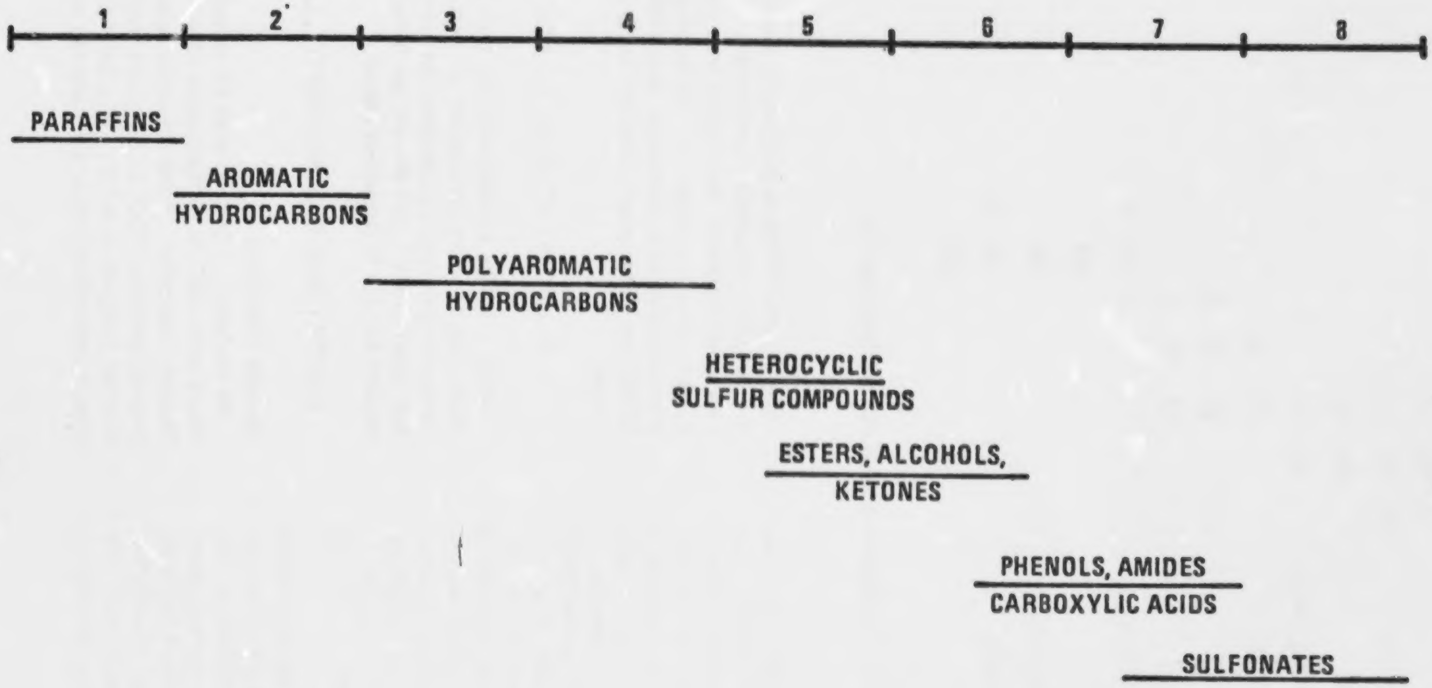


Figure 3. Liquid chromatographic fractions v. class types.

COMPOUND	1	2	3	4	5	6	7	8
HEXADECANE	85	15						
CUMENE		82	17					
DICHLOROBIPHENYL	25	69	5					
ACENAPTHENE		69	31					
TETRACHLOROETHANE		81	19					
o-NITROTOLUENE			30	70				
BENZALDEHYDE			22	75	3			
DIHEXYL ETHER			18	77	4			
N-METHYL ANILINE					3	94	2	
QUINOLINE						100		
DIETHYL PHTHALATE						100		
2-ETHYL HEXANOL						99	0.7	
PHENOL						100		

Figure 4. % Distribution in LC fractions (ref. 9).

is 700. A $1600 cost increase on 700 samples amounts to $1.7 million. In fact, since four of the seven SASS subsamples usually contain no significant amount of organic material, the expensive part of the scheme is seldom reached. The potential worst case cost must, nonetheless, be seriously considered.

The second strategical problem encountered when considering LRMS for inclusion in Level 1 is that the technique appears to be an "overkill" approach to what was originally a very modest analytical goal. In other words, one probably doesn't need that much information at Level 1 in order to make the necessary decisions. At present, LRMS is included in Level 1 as an option to be used on an "as needed" basis.

It should also be briefly discussed why LRMS is employed rather than the more powerful high resolution mass spectrometry (HRMS) or the more popular gas chromatography/mass spectrometry (GCMS). HRMS is roughly 4 times as expensive as LRMS. The detailed information and compound specificity available from this technique are far beyond the original goal of Level 1, and HRMS is not readily available for the quantity of samples envisioned. GCMS is also more expensive than LRMS and it has the added disadvantage of detecting only chromatographable materials. Both HRMS and GCMS are considered excellent Level 2 techniques.

ILLUSTRATIVE LEVEL 1 DATA

Level 1 SASS subsamples will typically involve results from extraction of particulate, porous polymer, or condensate. An example of this type of data for an electric arc furnace particulate sample is discussed below.

ELECTRIC ARC FURNACE PARTICULATE

Sample Treatment

Particulate (11.500 g) was extracted for 8 hours with 100 ml of methylene chloride in a Soxhlet extractor. Total chromatographable organic analysis (TCO) of the crude extract indicated 1 mg/ml of the C_7 - C_{16} boiling range. Gravimetric (Grav.) analysis indicated an addi-

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tional 13.8 mg of organic material present in the extract. The initial TCO + Grav. showed that the sample could be taken to dryness in the later steps of Level 1 without significant loss of sample.

TABLE 1

LEVEL 1 LC COLUMN RECOVERIES

Fraction	Weight, mg
1	7.2
2	1.5
3	2.0
4	1.9
5	1.8
6	3.3
7	1.4
8	0.1

Sample Fractionation

The recovered weights of material from the Level 1 LC column, that resulted from applying the total extracted sample (evaporated to dryness), are given in Table 1.

Infrared Analysis

Infrared results from fraction 6 were the most valuable. Strong or medium bands are reported in Table 2 with their assignments.

The IR of fraction 1 contained only hydrocarbon bands. The spectrum of fraction 3 contained bands at 2925, 2915, and 2830 cm^{-1}, indicative of aliphatic substitution. Infrared analysis of fractions 3 through 7 showed that the organic content of the sample was aromatic in nature with a variety of functional groups including multiple ring structures and oxidation products such as ketones and acids. No LRMS was performed on these samples since the quantity of material in any of the fractions was less than the threshold amount.

CONCLUSION

The objective in Level 1 organic analysis is to provide a cost effective screening scheme for source assessment. The electric arc furnace particulate example above shows many of the benefits of this approach. In particular, that all

TABLE 2

INFRARED BAND ASSIGNMENTS (FRACTION 6)

Band, cm^{-1}	Assignment
3500	A broad band indicating hydroxyl.
1710	Aromatic or conjugated ketone.
1510	Aromatic carbon stretch.
1455, 1460, 1380	Carbon/carbon scissor and wag.
830, 750	Substituted aromatic.

fractions from the LC separation after the second fraction are aromatic in nature and that the boiling point range for the sample is greater than C_{16} shows that the source potentially emits polycyclic organic material (POM) in the toxic and carcinogenic range. The weight and class distribution in the fraction causes the source to be of further interest. Level 2 analysis is indicated for POM by GC/MS or HPLC in combination with LRMS or HRMS.

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APPENDIX A
SELECTED LEVEL 1 PROCEDURES

A.1 *Procedure for Liquid Chromatography Column Preparation*

Column:	200 mm x 10.5 mm ID, glass with Teflon stopcock.
Adsorbent:	Davison Silica Gel, 60-200 mesh, Grade 950, (Fisher Scientific Company). This adsorbent is activated at 110°C for 2 hours just prior to use. Cool in a desiccator.

A.1.1 Dry-pack the chromatographic column, plugged at one end with glass wool, with 6.0 g of freshly activated silica gel. A portion of properly activated silica gel weighing 6.0 ± 0.2 g occupies 8 ml in a 10 ml graduated cylinder. Vibrate the column for 1 minute to compact the gel bed. Pour pentane into the solvent reservoir positioned above the column and let the pentane flow into the silica gel bed until the column is homogeneous throughout and free of any cracks and trapped air bubbles*. The total height of the silica bed in this packed column is 10 cm. The solvent void volume of the column is 2 to 4 ml. When the column is fully prepared, allow the pentane level in the column to drop to the top of the silica bed so that the sample can be loaded for subsequent chromatographic elution.

Table A1 shows the sequence of the chromatographic elution. In order to ensure adequate resolution and producibility, maintain the column elution rate at 1 ml per minute.

A.1.2 *Loading Sample on the Column*

Place 1 - 5 ml of CH_2Cl_2 extract containing 15 - 100 mg (preferably 100 mg) of solute (TCO + GRAV) in a graduated centrifuge tube or K-D receiver. Add 200 mg of silica gel prepared as for the LC column. Evaporate if necessary to reduce volume to 1 ml. Add 1 ml of hexane and mix by gentle agitation. Again reduce the volume to 1 ml by evaporation. Add 1 ml more of hexane and mix. Again reduce the volume to 1 ml. Transfer the hexane and silica gel to the top of the previously prepared LC column.

Run the column as directed, rinsing the graduated receiver with fresh solvent as they are introduced in the elution sequence.

A.1.3 *Chromatographic Separation into Eight Fractions*

The volume of solvents shown in Table A1 represents the solvent volume collected for that fraction. If the volume of solvent collected is less than the volume actually added due to evaporation, add additional solvent as necessary. In all cases, however, the solvent level in the column should be at the top of the gel bed (i.e., the sample-containing zone) at the end of the collection of any sample fraction.

After the first fraction is collected, rinse the original sample, weighing the funnel with a few ml of the fraction 2 solvent (20% methylene chloride/pentane) and carefully transfer this rinsing into the column. Repeat as necessary for fractions 3 and 4.

A.2 *Total Chromatographable Organic Analysis (TCO)*

Analyze a l μl aliquot of solution by GC using a flame ionization detector. A 6 ft x 1/8 in. O.D. column of 10% OV-101 on 100/120 mesh Supelcoport has been used successfully for this analysis. Other silicon phases (OV-1, etc.) may work as well, but a 10% loading is recommended. The GC should be operated isothermally at about 30° C — or room temperature — for 5 minutes after sample injection and then programmed at approximately 20°C per minute to 250°C and held at 250°C as long as necessary for complete elution of sample.

Integrator should be set to begin integration at a time intermediate between the hexane (C_6) and heptane (C_7) peak maxima (i.e., $C_{6.5}$) and terminate at the peak maxima of the heptadecane (C_{17}) peak, as determined from calibration standards. In this manner the integrated area will cover material in the boiling range of C_7 - C_{16}.

Calibration should utilize a mixture containing a homologous series of hydrocarbons from C_7 to C_{16}. Standards should be prepared to cover the concentration range to be studied.

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*A water jacketed column run between 18 and 22°C will help avoid this problem.

TABLE A1

LIQUID CHROMATOGRAPHY ELUTION SEQUENCE

No. Fraction	Solvent Composition	Volume Collected, ml
1	Pentane	25
2	20% Methylene chloride in pentane	10
3	50% Methylene chloride in pentane	10
4	Methylene chloride	10
5	5% Methanol in methylene chloride	10
6	20% Methanol in methylene chloride	10
7	50% Methanol in methylene chloride	10
8	Conc. HCl/Methanol/Methylene chloride (5 + 70 + 30)	10

ENVIRONMENTAL ASPECTS OF FOSSIL ENERGY DEMONSTRATION PLANTS

James C. Johnson
Energy Research and Development
Administration
Washington, DC

Abstract

This paper described the full range of environmental activities which are undertaken in conjunction with Fossil Energy's demonstration plant program. These activities address key environmental problems generic to any Fossil Energy demonstration plant: resource limitations (e.g., water availability), socioeconomic impacts (e.g., housing shortages); new and potentially harmful pollutants; existing environmental standards; and future environmental standards.

In order to provide a background for the discussion of specific environmental activities, the paper first described the overall Fossil Energy Demonstration Program, including program objectives, ERDA's role, industry's role, and funding. The paper then defined the three developmental phases of demonstration plants (Phase I: preliminary and detailed plant engineering; Phase II: plant construction; and Phase III: plant operation, testing, and evaluation), since specific environmental activities occur at each phase.

During Phase I, environmental activities include the preparation of site specific environmental impact assessments (EIS's) and/or environmental impact statements (EIS's), development of environmental control strategies, design of environmental monitoring and control systems, compilation and review of public comments, and securing of necessary permits. During the design phase data describing ambient environmental conditions at prospective sites also are collected.

During Phase II, environmental monitoring and control systems are constructed for inclusion in the demonstration plant. During construction ambient air and water quality data are collected in order to assess the impacts of construction on the local environment. Worker health and safety surveillance programs are established, and potentially hazardous plant areas are pinpointed.

A comprehensive program to monitor air emissions, water effluents, and worker health and safety is implemented during Phase III. A comparison of air and water monitoring data with background ambient data collected during Phase I will allow changes in the local environment to be assessed. Data also are collected to ensure compliance with environmental standards, and tests are carried out which will lead to improvements in environmental control technology.

PROTECTING WORKER SAFETY AND HEALTH IN COAL CONVERSION

Murray L. Cohen
National Institute for
Occupational Safety and Health
Rockville, Maryland

Abstract

The National Institute for Occupational Safety and Health (NIOSH) is responsible for developing recommended standards for occupational exposures to chemical and physical hazards, including those which arise in newly developing technology. An assessment of the potential deleterious impact on the occupational environment by coal conversion technologies is in progress, including the identification of possible hazardous exposures to workers and the development of strategies for control of these exposures.

NIOSH has developed occupational safety and health guidelines for coal gasification pilot plants and is preparing recommended standards for coal conversion processes that will likely be commercialized in the U.S. by 1985. The methodology includes a world-wide literature survey, visits to operational facilities, and evaluation of the occupational safety and health practices and records in coal conversion plants.

A unique process orientation forms the basis of the occupational safety and health recommendations, with emphasis on real-time monitoring of indicator substances to identify problem areas and fugitive emissions. Engineering controls, safe work practices, industrial and personal hygiene, medical examinations and recordkeeping, and personal protective equipment complete the recommended standard.

The need to simultaneously develop control technology and advance process engineering for coal conversion technologies is evident. Potential occupational health and safety problems can be prevented by proper attention to these considerations in the design of synfuel plants.

PROTECTING WORKER SAFETY AND HEALTH IN COAL CONVERSION

The National Institute for Occupational Safety and Health (NIOSH) is responsible for developing recommended standards for occupational exposures to chemical and physical hazards, including those which arise in newly developing technology. Since April 1976, the Institute has been involved in a project to identify potential hazardous exposures to workers in coal gasification plants. Strategies for control of these exposures are also being developed.

The project has been divided into two parts. *Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants* have been developed, and will be transmitted to the Energy Research and Development Administration (ERDA) later this year for consideration for implementation in the ERDA research and development facilities. In August, work began on the *Criteria for Recommended Standards for Occupational Exposures in Coal Gasification Plants.* This NIOSH criteria document will address coal gasification processes that will likely be commercialized in the United States by 1985. In May 1978, the recommended standards will be transmitted to the Department of Labor Occupational Safety and Health Administration for consideration for rulemaking.

It is important to note that the development of criteria documents includes substantial review at five different stages of drafting. Reviewers include NIOSH staff and consultants, other federal and state agencies, and representatives of industry, labor unions, and academia.

The protocol followed in the development of each of these documents includes a world-wide literature survey and review, visits to operational facilities, and evaluation of the occupational safety and health practices and records in coal gasification plants. The recommendations for control of hazardous exposures have in all cases been based upon the operational experiences of existing facilities. Similar data from industries with analogous exposures, such as coke ovens and coal liquefaction plants, have also been considered in the identification of potential hazards to workers.

A process oriented approach is being used in the development of these recommended standards, as opposed to the more traditional single hazard approach. The processes are divided into operational units characterized by certain hazards. Recommendations for control of exposures are then designed in unit packages that are specific for each process unit. The recommendations emphasize real-time monitoring of indicator substances to identify problem areas and fugitive emissions. Engineering controls, safe work practices, industrial and personal hygiene, medical examinations and recordkeeping, and personal protective equipment complete the recommendard standard.

PILOT PLANT DOCUMENT

The pilot plant worker may be exposed to toxicants by inhalation of gases or airborne particles, skin deposition of airborne material, contact with contaminated surfaces and accidental ingestion. In maintenance operations, liquid and solid residues may be encountered that would not ordinarily constitute normal operational hazards (NIOSH 1977).

The range of toxicants and possible health effects is extremely wide, from simple chemicals like carbon monoxide to complex mixtures of organic carcinogens. This complexity is further complicated by the special problems associated with carcinogens: long latent period, doubt about "safe" levels, and unpredictable multiagent interactions (NIOSH 1977).

These conditions cannot be met by protective measures, monitoring procedures, and medical tests that are simply the sum total of controls for each individual toxicant. The complexity of the potential hazards calls for innovative control strategies (NIOSH 1977).

Few data are available concerning the workplace environment and other occupational health factors in coal gasification plants. The somewhat better documented health hazards of coke ovens, coal liquefaction, and similar plants are relevant, but not fully acceptable as models for coal gasification (NIOSH 1977).

The structure of the document includes a detailed description of a representative process, identification of toxicants and potentially hazardous operations, a review of health effects associated with the toxicants and diseases observed in association with coal processing, recommendations for worker protection, monitoring procedures, safety considerations, and recommendations for research to meet identified gaps in knowledge and technology for worker health and safety protection.

The coal gasification processes used as references are seen in Table 1. Synthane is the representative process for development of control strategies, and significant differences or unique characteristics of the other processes are noted in the document.

The unit processes for which specific control strategy packages have been developed are coal preparation, pretreatment and gasification, quench and scrubbing, CO shift conversion, acid gas scrubbing, methanation, sulfur recovery and waste water treatment, and the handling of condensable hydrocarbons, ash, and char.

Health effects data that serve as the basis for the recommendations are reviewed for the following toxicants:

- Aliphatic hydrocarbons
- Ammonia
- Aromatic Amines
- Aromatic hydrocarbons
- Arsine
- Carbon disulfide
- Carbon monoxide
- Carbonyl sulfide
- Heterocyclic aromatics
- Hydrogen chloride
- Hydrogen cyanide
- Hydrogen sulfide
- Mineral dust and ash
- Nickel carbonyl
- Nitrogen oxides
- Nitrosamines
- Phenols
- Polycyclic aromatic hydrocarbons
- Sulfur oxides
- Trace elements

Other types of data essential for develop-

TABLE 1

COAL GASIFICATION SYSTEMS USED AS REFERENCES

			Product			Status	
Process	Pressure, psig	Temperature, °F	Gas Quality	Liquids	Coal Feed	(Dec. 1976)	Type
HYGAS, Steam-Oxygen	1000[a] 1000-1500[c]	1300-1900	Medium or high	Light oil and tar	Lignite Sub-bituminous Bituminous[b]	Operational	Pilot
CO_2 Acceptor	150[a] 150-300[c]	1500-1850[d]	Medium or high	None	Lignite Sub-bituminous	Operational	Pilot
MERC Unit	200[a] Atmos-300[c]	Combustion zone 2400-2500 Gas off take 1000-1200	Low, medium, or high	Light oil and tar	Lignite Sub-bituminous Bituminous	Operational	Pilot
Synthane	1000[a] 600-1000[c]	1500[a] 1400-1800[c]	Medium or high[e]	Light oil and tar	Lignite Sub-bituminous Bituminous[b]	Start-up	Pilot
Bi-Gas	Upper stage (entrained flow) 1000-1500 Lower stage (vortex flow) 1000-15000	1400-1700 2800	Medium or high[e]	(Doubtful)	Lignite Sub-bituminous Bituminous	Start-un	Pilot
Agglomerating Burner	Atmos-100	1800	Medium or high	(Questionable)	Lignite Sub-bituminous Bituminous[b]	Start-up	PDU
Steam-Iron	1000-1200	Hydrogasifier 1300-1700 Producer 2000-3000	Hydrogen	None	Char	Under construction	Pilot

[a] Normal operating pressure.

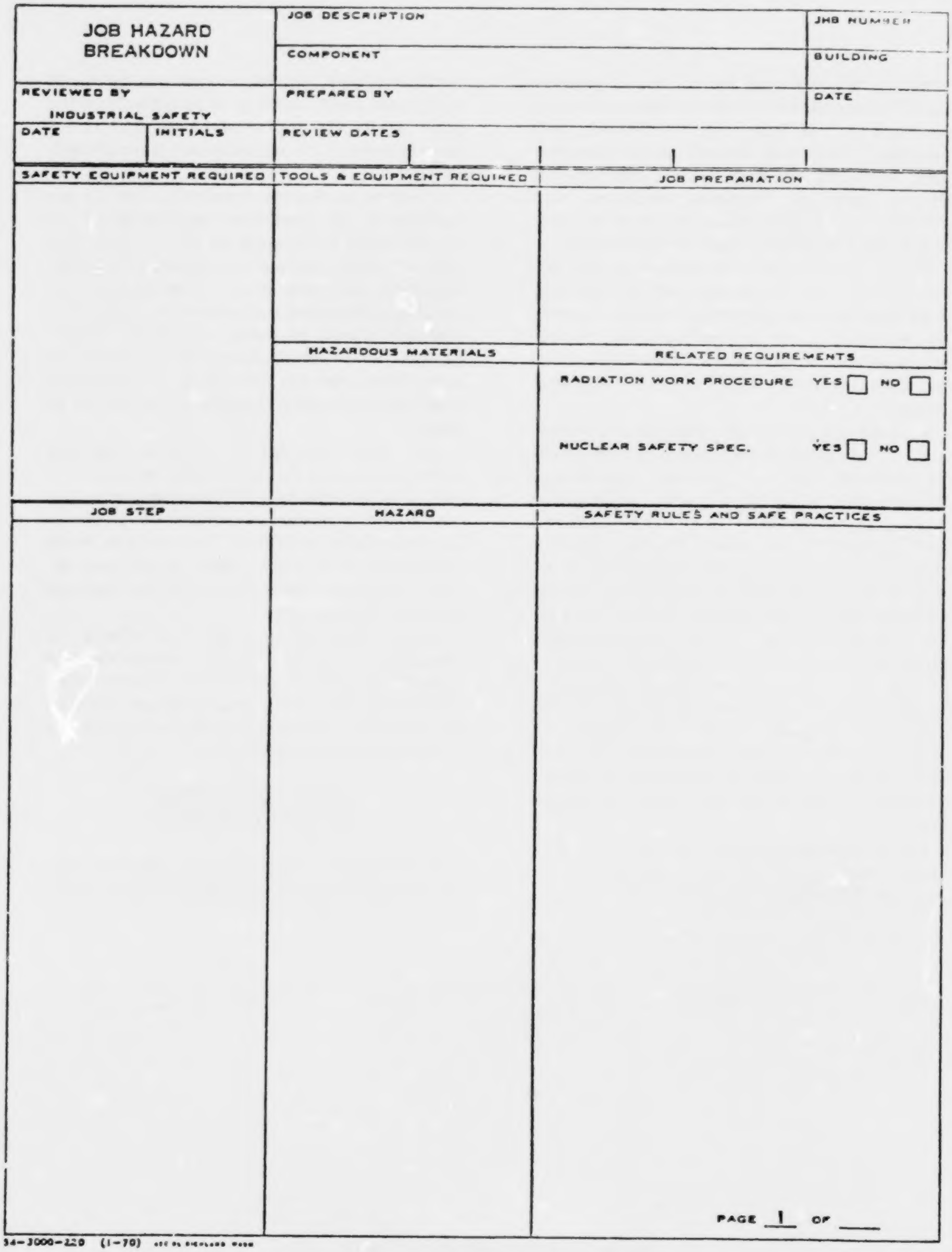
[b] Must pretreat agglomerating bituminous coal.

[c] Optimal range.

[d] Coal bed 1500°F, regenerator 1840°F.

[e] Can be converted to low-Btu gas production.

Source: NIOSH Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants.



JOB HAZARD BREAKDOWN	JOB DESCRIPTION	JHB NUMBER
	COMPONENT	BUILDING
REVIEWED BY INDUSTRIAL SAFETY	PREPARED BY	DATE
DATE | INITIALS	REVIEW DATES	

SAFETY EQUIPMENT REQUIRED	TOOLS & EQUIPMENT REQUIRED	JOB PREPARATION
	HAZARDOUS MATERIALS	RELATED REQUIREMENTS
		RADIATION WORK PROCEDURE YES ☐ NO ☐
		NUCLEAR SAFETY SPEC. YES ☐ NO ☐

JOB STEP	HAZARD	SAFETY RULES AND SAFE PRACTICES

PAGE 1 OF ____

54-3000-220 (1-70) [illegible]

Figure 1. Job safety analysis sample form.

ment of recommendations on a unit process basis include health effects studies for the coal liquefaction and coke oven industries, and engineering data that serve to predict potential problem areas in coal gasification plants. Stream analyses, material balances, and process flow sheets from the existing pilot plants were extremely useful in this regard.

Recommendations for worker protection are prescribed in the document, and include safe work practices, engineering controls, protective equipment, workplace monitoring, medical examinations, recordkeeping, health education program, personal hygiene, and regulated areas.

Figure 1 is a sample job safety analysis form, and represents a safe work practice that should be required for all routine operations. Maintenance tasks should also include safe work permits signed in advance by both the shift supervisor and safety officer. Figure 2 shows a sample pump and shutoff valve arrangement that constitutes a simple but highly effective engineering control. Medical monitoring should include a full preemployment physical, regular checkups, long-term followup of high risk individuals, and full recordkeeping for all workers in the plant. An effective health education program must both teach the employees the hazards associated with their work, and continually remind them of the importance of the health and safety protection program.

Figure 3 is a sample layout for clean and dirty locker rooms that can assure good personal hygiene. The important points are that no contaminated work clothing or gear can be mixed with clean street clothing, or be taken from the plant facility. Figure 4 shows signs that can be used to enforce the regulated areas recommendations.

Effective workplace monitoring can be accomplished by continued monitoring of indicator substances such as CO or H_2S. This concept allows for real-time detection of leaks, indicates the time when measurements of specific substances that cannot be analyzed in real-time should be made, and easily "flags" periods when precautions for exposure to substances that are difficult or impossible to analyze at prevailing concentrations should be taken.

The characteristics of a good indicator substance are as follows: easily monitored in real-time, suitable for analysis where resources are limited, presence in ambient air at low or consistent concentrations, free from interfering substances in process stream or ambient air, and a regulated agent that must be measured anyway (NIOSH 1977).

These characteristics are the criteria for choosing a specific indicator substance in a specific process or work area. "Tailor-made" workplace monitoring programs can then be developed according to process conditions in a specific coal gasification plant.

COAL GASIFICATION CRITERIA DOCUMENT

This program is just getting underway, with an anticipated publication date of June 1978.

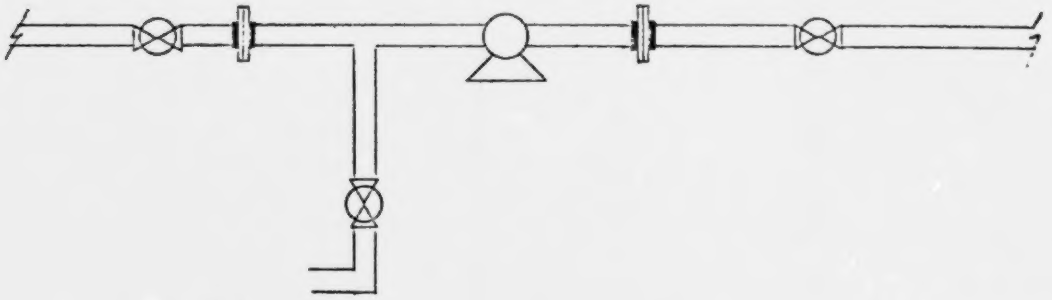


Figure 2. Pump and shutoff valve

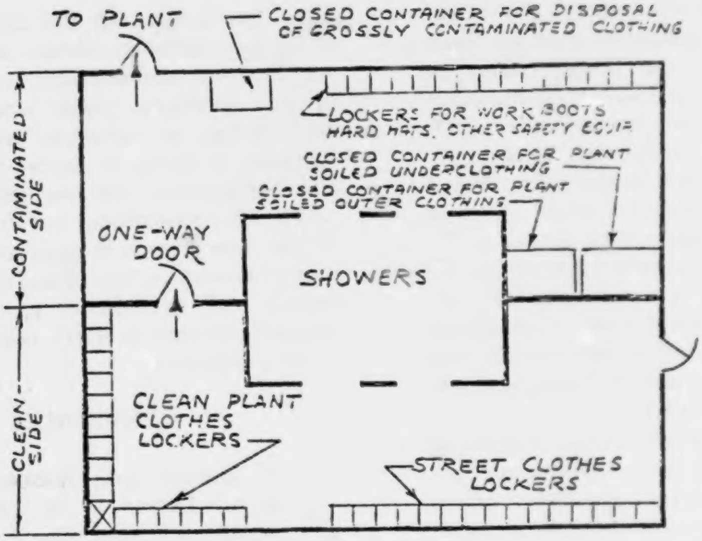

TO PLANT
CLOSED CONTAINER FOR DISPOSAL OF GROSSLY CONTAMINATED CLOTHING
LOCKERS FOR WORK BOOTS HARD HATS, OTHER SAFETY EQUIP
CLOSED CONTAINER FOR PLANT SOILED UNDERCLOTHING
CLOSED CONTAINER FOR PLANT SOILED OUTER CLOTHING
CONTAMINATED SIDE
ONE-WAY DOOR
SHOWERS
CLEAN SIDE
CLEAN PLANT CLOTHES LOCKERS
STREET CLOTHES LOCKERS

Figure 3. Sample layout for clean and dirty locker rooms.

CAUTION

Restricted Area

Authorized Employees Only

CAUTION

Cancer Suspect Agents

Respiratory Protection Required

Authorized Employees Only

Figure 4. Sample signs for regulated areas.

The criteria document will focus on the following coal gasification processes that will likely be commercialized in the United States by 1985: high-BTU (LURGI), low-BTU (bituminous or lower grade coals), and low or medium-BTU (anthracite or non-tar producing). Hazard control recommendations will be developed from a unit process perspective for each of these classes of operation and will be similar to the types of recommendations developed for the pilot plants. Since few commercial coal gasification facilities are currently operational in the U.S., the recommendations will emphasize engineering controls and design criteria for built-in margins of safety.

It is hoped that these NIOSH documents will serve as handbooks for use in developing effective comprehensive safety and health programs in the building of the coal gasification industry. The philosophy of the program is based on the principle that before a new technology is introduced or an existing technology is modified, its occupational health and safety impact should be evaluated. Historically, advances in technology have been accompanied by new hazards which are often apparent only many years later, after workers become sick or die. The styrene-butadiene rubber industry is an example. In the 1940's, with 90 percent of the natural rubber supply cut off, the Federal government financed the building of fifteen styrene-butadiene rubber plants (Morton, 1973). Three decades later, we are finding that styrene-butadiene rubber employees have a six-fold risk, as compared with other rubber workers, of dying of cancer of the lymphatic and hemopoietic systems (McMichael et al. 1976). If occupational health and safety are properly considered in developing coal conversion technologies, then these plants, hopefully, should not contribute to serious health problems twenty to thirty years from now for today's workers.

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ENVIRONMENTAL RESEARCH RELATED TO FOSSIL FUEL CONVERSION

by

Gerald J. Rausa
Environmental Scientist
Energy Coordination Staff
Office of Energy, Minerals, and Industry
U.S. Environmental Protection Agency
Washington, D.C. 20460

Abstract

The taxonomy of environmental research developed by the CEQ-OMB Interagency Working Group on Health and Environmental Effects of Energy Use is used to convey the ongoing environmental research related to conversion of solid fossil fuels to liquids and/or gases. The inventories of activities in the interagency (pass-thru) program and in the base programs of the contributing agencies is discussed. Research for all modules of the fuel cycle is addressed. As a consequence, some research which is generally applicable to all fossil fuel cycles is included in the discussion.

INTRODUCTION

Some difficulty is encountered in the attempt to categorize the environmental research which is solely applicable to fossil fuel conversion, since some aspects of environmental research are related in common to a number of industries, including the energy industry and its associated technologies. In particular, the various fossil fuel conversion cycles have problems in common with other fuel cycles as well as having technology-specific problems. In order to convey the scope of environmental research related to fuel conversion (liquefaction or gasification), it is appropriate to discuss the generally applicable environmental research as well as that which is process-specific.

It is debatable whether or not energy related environmental research can be partitioned into mutually exclusive categories that are acceptable to all interested parties. For example, one such grouping of tasks could be according to environmental agents, i.e., physical, chemical, and biological stressors. Another possibility could be a sorting according to the environmental media into which the agents are initially introduced, i.e., air, water, and land. A third sort could be according to the targets of concern, i.e., human health, environmental quality, ecological systems, social systems or economic systems.

In this presentation, the taxonomies developed by the two OMB-CEQ working groups(1,2) in the planning of energy related enviromental research will be used to categorize the research activity to be discussed. The subject working groups were assembled to respond to an inquiry as to whether or not energy related environmental research was being undertaken on a schedule compatible with the development of energy technology, and to indicate the additional environmental research needed. The categories utilized by the two working groups are displayed in Figure . The "Gage Committee" addressed the engineering aspects of control systems while the "King/Muir Committee" addressed the environmental processes and effects aspects of the energy systems. The categories were developed by the interagency working groups to provide a planing structure that could be used by each agency in order to permit the individual components of activity to be aggregated within the overall interagency (pass-thru) program, while still permitting each agency to fit the "pass-thru" component within its own base program structure. In essence, the interagency program is supplemental to the base programs of energy related environmental research of the individual agencies.

The interagency planning structure is depicted in Figure 2. For each major fuel cycle, the additional research needs for the working groups were listed for each module of the cycle. Common problems and pertinent research requirements were then aggregated and priorities were established according to the following major processes and effects categories:

1. *Pollutant Characterization, Measurement and Monitoring* (CM&M)

The objective of this research is to provide

ENERGY/ENVIRONMENT RESEARCH AND DEVELOPMENT PROGRAM

GAGE REPORT ENVIRONMENTAL CONTROL TECHNOLOGY	KING-MUIR REPORT HEALTH AND ENVIRONMENTAL EFFECTS
ENERGY RESOURCE EXTRACTION	POLLUTANT CHARACTERIZATION, MEASUREMENT AND MONITORING
PHYSICAL AND CHEMICAL COAL CLEANING	ENVIRONMENTAL TRANSPORT PROCESSES
FLUE GAS CLEANING	ECOLOGICAL EFFECTS
DIRECT COMBUSTION	HEALTH EFFECTS
SYNTHETIC FUELS	INTEGRATED ASSESSMENT
NUCLEAR	
THERMAL	
IMPROVED EFFICIENCY	
ADVANCED SYSTEMS	

Figure 1. OMB-CEQ working groups on energy-related environmental research.

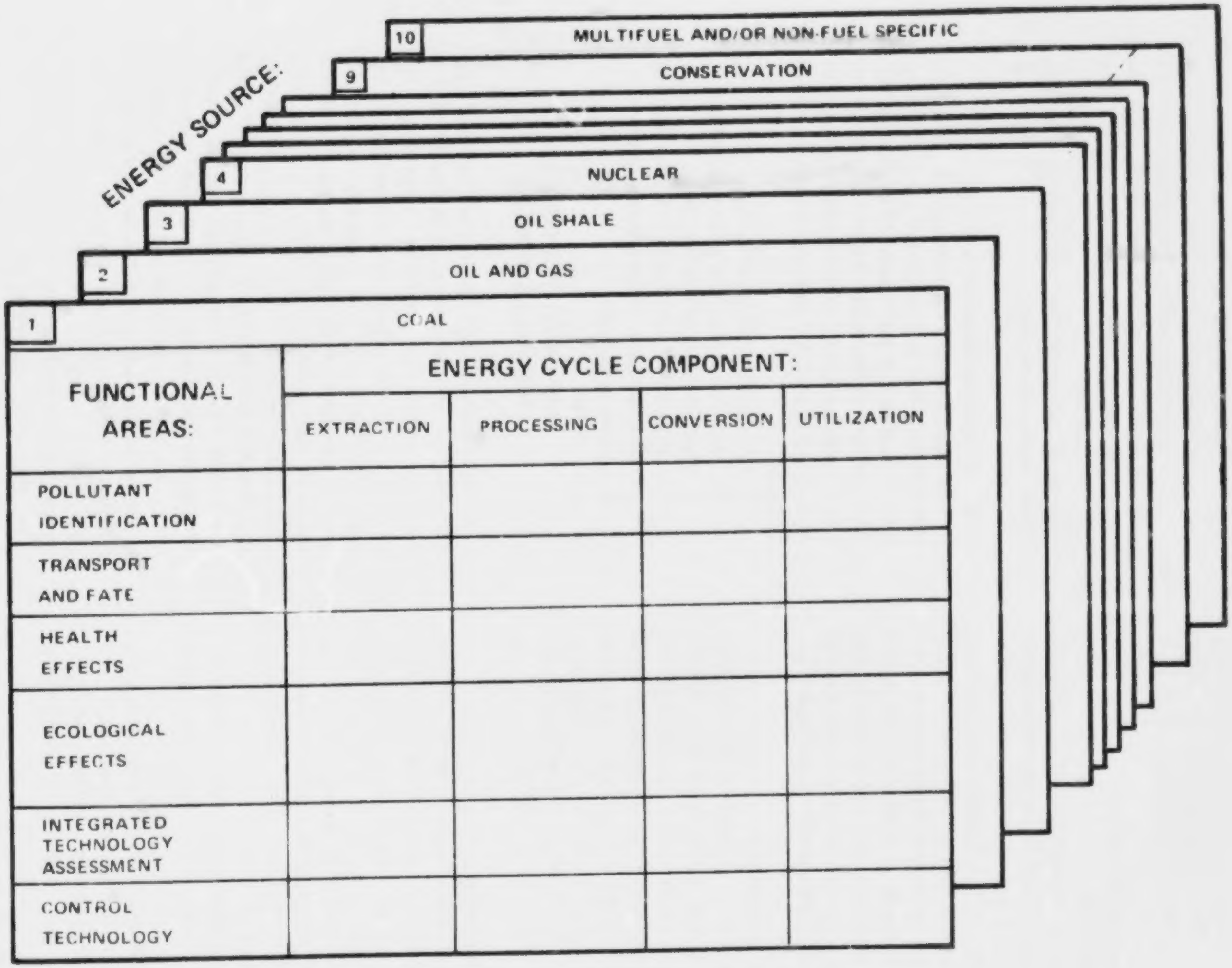

ENERGY SOURCE:
10 MULTIFUEL AND/OR NON-FUEL SPECIFIC
9 CONSERVATION
4 NUCLEAR
3 OIL SHALE
2 OIL AND GAS
1 COAL
ENERGY CYCLE COMPONENT:
FUNCTIONAL AREAS:
EXTRACTION
PROCESSING
CONVERSION
UTILIZATION
POLLUTANT IDENTIFICATION
TRANSPORT AND FATE
HEALTH EFFECTS
ECOLOGICAL EFFECTS
INTEGRATED TECHNOLOGY ASSESSMENT
CONTROL TECHNOLOGY

Figure 2. Interagency planning structure.

reliable and accurate measures of the quantities and characteristics of released pollutants, transformed products and indices of environmental impacts. The major subcategories of research include instrumentation development, source characterization, ambient monitoring and quality assurance.

2. *Environmental Transport Processes* (ETP)

The objective of research in this category (also occasionally titled Pollutant Transport, Transformation and Fate - TT&F) is to provide reliable estimates of the spatial and temporal relationships between emissions and ambient environmental quality which represents the exposures to the targets of concern. The major categories of research include atmospheric pathways, aquatic pathways, terrestrial pathways, and biological pathways (Figure 3).

3. *Ecological Effects* (EE)

The objective of this research is to determine the acute and chronic impacts to ecosystems and the components thereof - specifically the nature and extent of response to various stimuli associated with energy production. The components of concern include the habitats, populations, and processes in the atmospheric, aquatic, and terrestrial ecosystems.

4. *Health Effects* (HE)

The objective of this research is to provide reliable qualitative and quantitative estimates of effects on human health due to energy related agents - for long term, low level exposure, for all modules of energy production and use, and for susceptible occupational and general population groups. The major subcategories of research include:

1. The development of more rapid indicators for dose and biological damage;
2. The identification of hazardous agents associated with energy systems;
3. The development of understanding of biological mechanisms of metabolism and fate;
4. The development of understanding of mechanisms of damage, repair, and recovery in biological systems from energy related agents;
5. The development of estimates of risk to human health evaluated through human health studies and animal toxicological studies, and by improvement of techniques for extrapolation of data from animal to man and from high levels of exposure to low levels of exposure.

Figure 4 indicates the relationships amongst these areas of research.

5. *Integrated Assessment* (IA)

The objective of this research is to provide the methods for, and to undertake comprehensive evaluation of the impact of energy production and use on the total "human environment" from local, regional, and/or national perspective. To this end the subcategories of activity include:

1. integration of information;
2. social and welfare effects analysis;
3. cost/risk/benefit evaluation;
4. analysis of alternative methods of implementation of strategies; and
5. siting analysis.

ENERGY/ENVIRONMENT PROGRAM EMPHASIS

Before elaborating upon the research applicable to fuel conversion, it is appropriate to convey some perspective regarding the magnitude of the effort, and the emphasis being undertaken for all federally supported, energy related environmental research which is listed in two available data files.[3,4] The data bases used for this perspective include the EPA coordinated interagency program data file and the ERDA FY-76 inventory of energy related environmental research. The ERDA inventory may not have captured all of the subject research tasks because of the lack of a precise definition of the phrase "energy related environmental research," and the subsequent interpretation of that phrase by the respondents.

In the EPA coordinated interagency environmental processes and effects program, the relative emphasis has remained reasonably

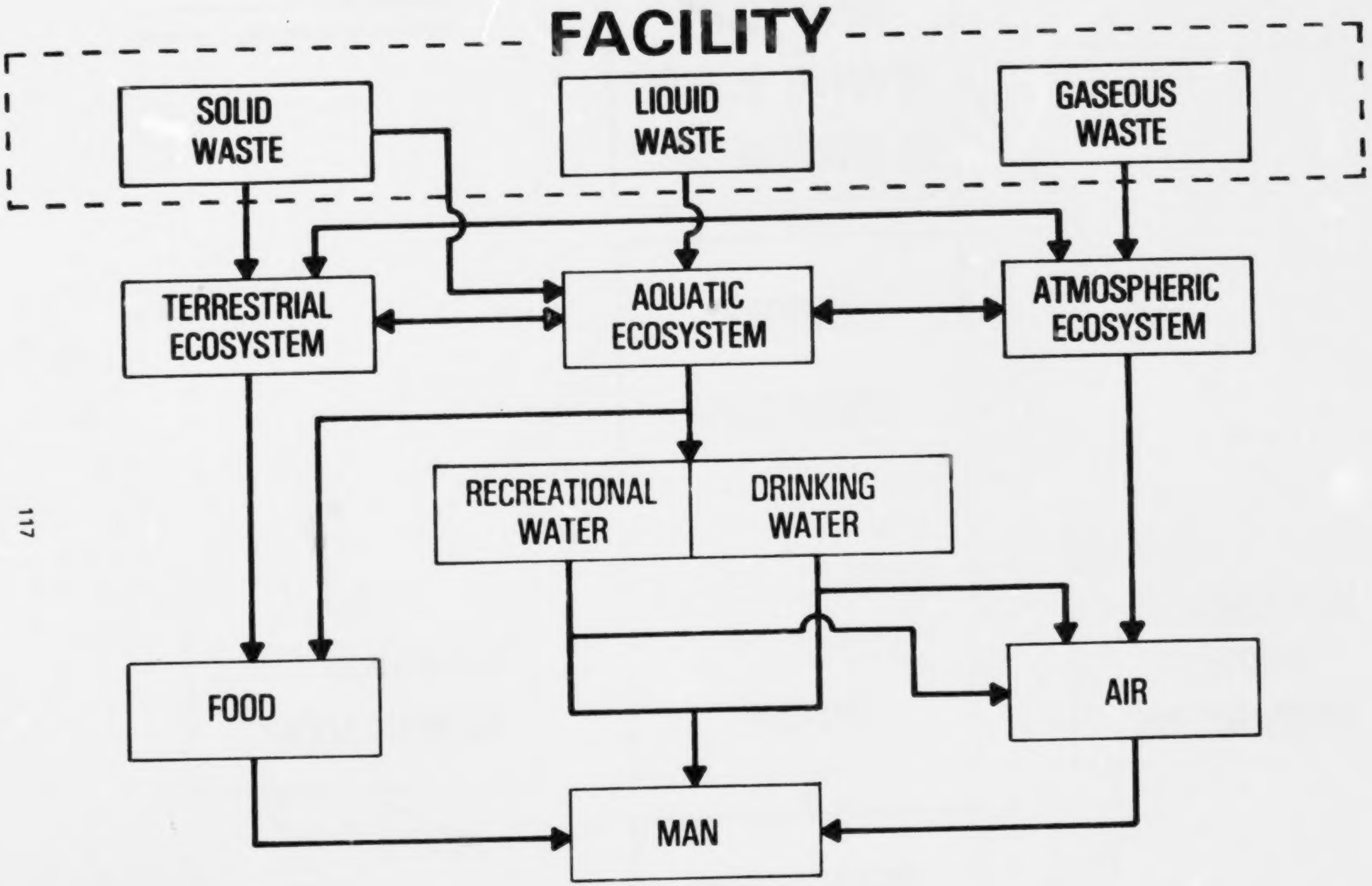

FACILITY
SOLID WASTE
LIQUID WASTE
GASEOUS WASTE
TERRESTRIAL ECOSYSTEM
AQUATIC ECOSYSTEM
ATMOSPHERIC ECOSYSTEM
RECREATIONAL WATER
DRINKING WATER
FOOD
AIR
MAN

Figure 3. Environmental pathways model.

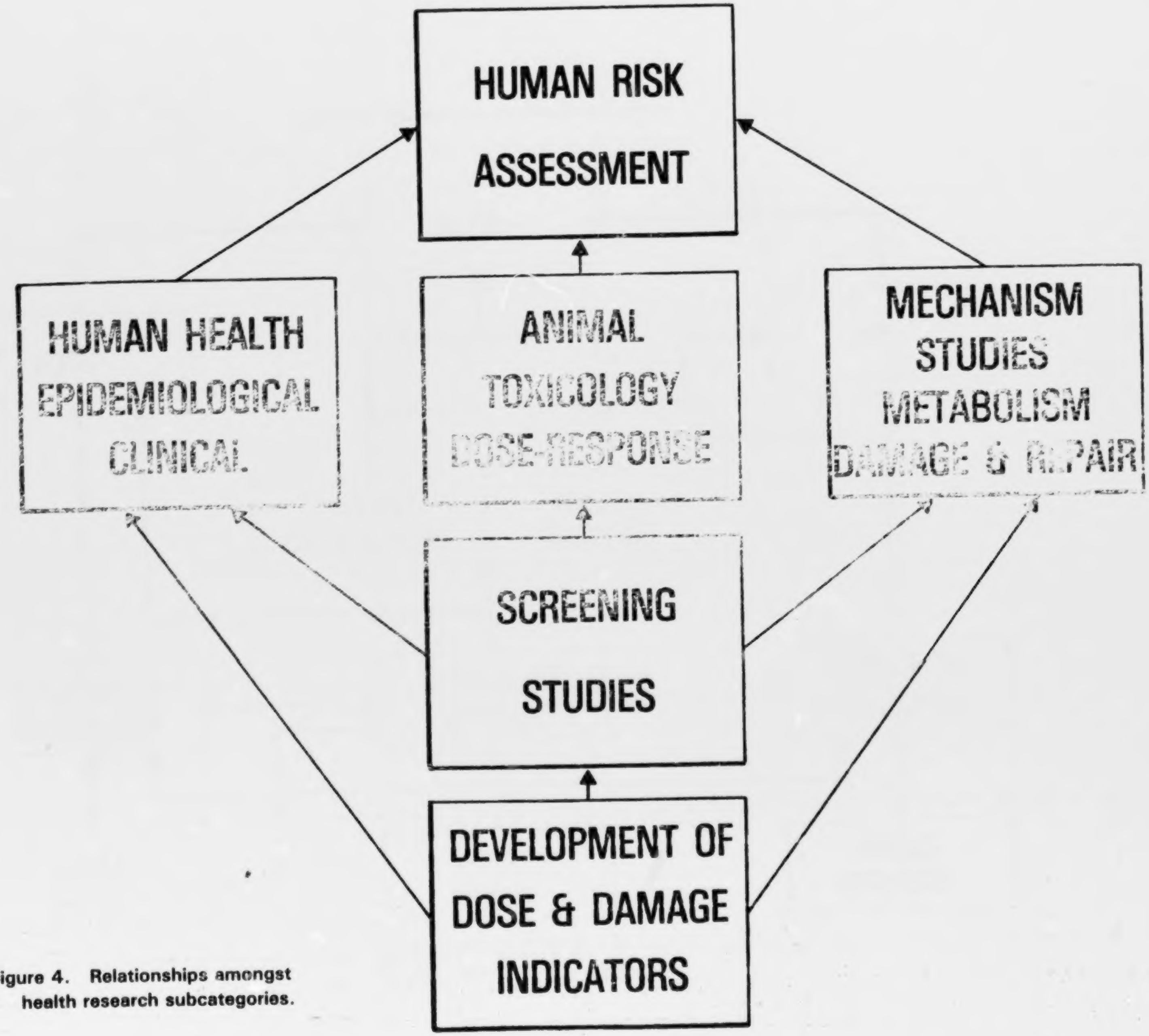

HUMAN RISK ASSESSMENT
HUMAN HEALTH EPIDEMIOLOGICAL CLINICAL
ANIMAL TOXICOLOGY DOSE-RESPONSE
MECHANISM STUDIES METABOLISM DAMAGE & REPAIR
SCREENING STUDIES
DEVELOPMENT OF DOSE & DAMAGE INDICATORS

Figure 4. Relationships amongst health research subcategories.

stable for FY-75, FY-76, and FY-77 (Figure 5), with the major emphasis, approximately 32 percent, upon health effects research. A comparable evaluation for the total energy related environmental research program (base programs and interagency pass-thru program), which was obtained from the ERDA FY-76 inventory, is displayed in Figure 6. Comparison to the pass-thru program indicates that the supplemental interagency effort increased the relative emphasis on measurement and monitoring and on ecological effects research.

Disaggregation of the relative emphasis (FY-76) of the interagency program, according to components of the fuel cycles for all energy systems, indicates a relatively uniform emphasis for extraction, processing, and utilization (Figure 7). For the base programs the emphasis according to the same modules is 23 percent, 15 percent, and 62 percent, respectively. The emphasis on utilization is related to the research to resolve the nuclear waste management problem.

The distribution of effort for all energy related environmental research, categorized according to energy technology, was displayed in the ERDA inventory and is reproduced in Figure 8. As expected, the major efforts are for nuclear and fossil systems with an additional component applicable to several fuel cycles. A similar analysis for the supplementary pass-thru program indicates that most of that particular funding has been allocated to research applicable to fossil fuel technologies.

A more comprehensive breakdown of the emphasis in environmental research applicable to fossil fuel technology for both the interagency pass-thru program and for the base programs is presented in Figure 9. The data indicate that, while approximately 46 percent of the base funding for processes and effects projects are related to fossil fuel technology, approximately 92 percent of the pass-thru program was applicable thereto, thus making 52 percent of the total FY-76 funding reported applicable to fossil fuel technology. The data indicate that the major emphasis and the largest number of projects being undertaken address health effects issues. On the other hand, the largest average cost per task is for ecological effects research, while the lowest average cost per task is for health effects research.

ENVIRONMENTAL RESEARCH FOR ADVANCED FOSSIL FUEL CYCLES

As suggested previously, the advanced fossil fuel cycles will require resolution of some problems in common with the conventional fossil fuel cycles. The problems in common are those primarily associated with the extraction and/or utilization module of the full cycle. Examples of such common problems include the following:

1. Impacts upon water quality due to mine drainage or leaching from disposal of solid waste, and subsequent impact upon aquatic ecosystems;
2. Impacts upon water supply associated with aquifier disruption (mining), revegetation requirements or slurry transport;
3. Impacts upon air quality and weather/climate modification (local and regional) from surface mining and combustion;
4. Impacts upon health related to coal dust and waste products of combustion (SO_x, NO_x, hydrocarbons, particulates, trace metals, organometallics), and their environmentally transformed products;
5. The need to develop measurement tools and techniques and obtain the baseline information for likely sites; and
6. Comparative evaluation of alternative futures for likely sites and the addressing of "boom town" problems.

Specific problems within each of the categories are as follows:

Characterization Measurement and Monitoring - the process specific concerns associated with advanced fossil fuels systems stems from the spectrum of agents anticipated to be associated with the variety of proposed processes and products. Of major concern is the variety of organic agents in the products and waste streams. An example of a variety can be seen in the chromatogram of a coal liquefaction product, made by M. Guerin of Oak Ridge National Laboratory,(5) is displayed in Figure 10. Il-

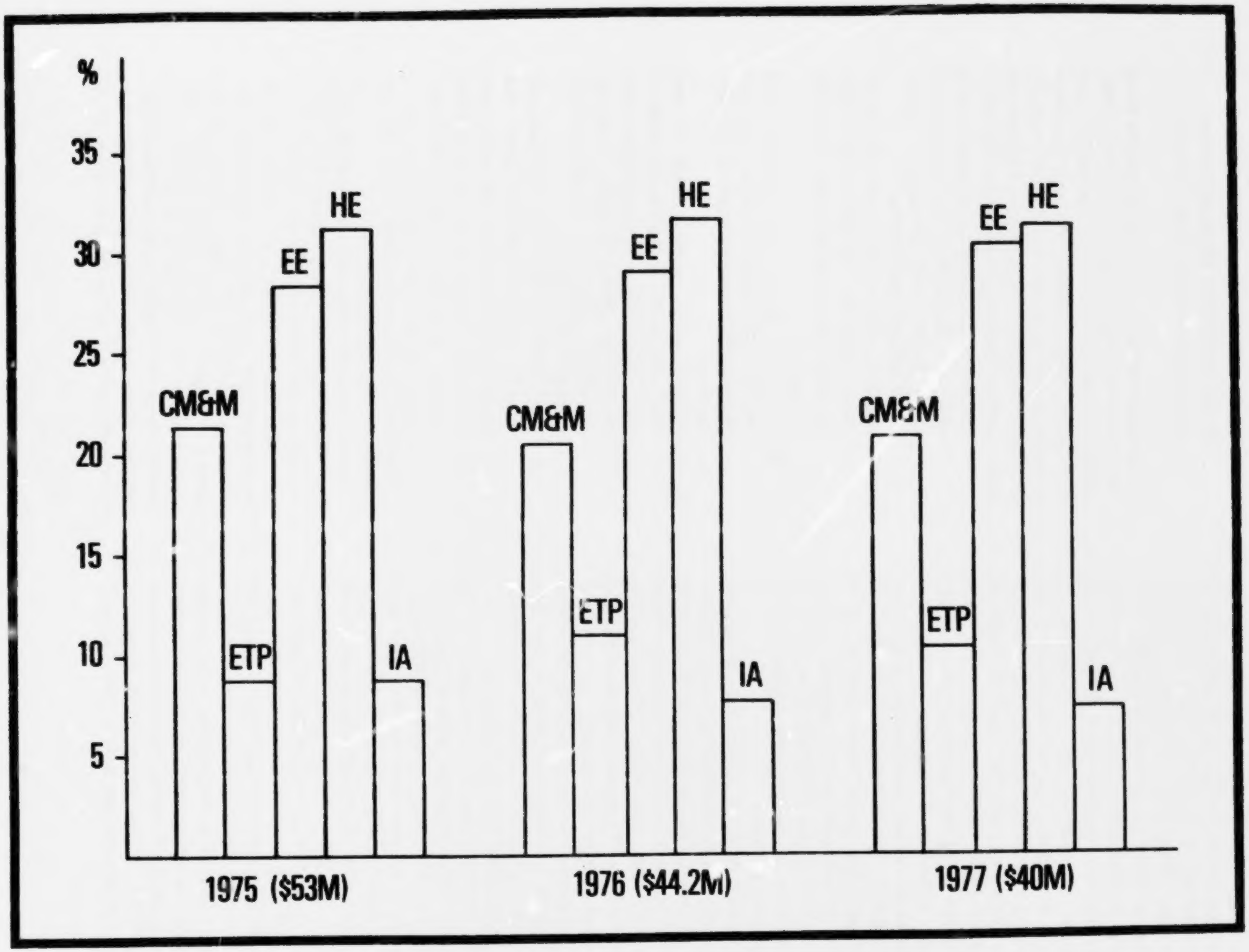
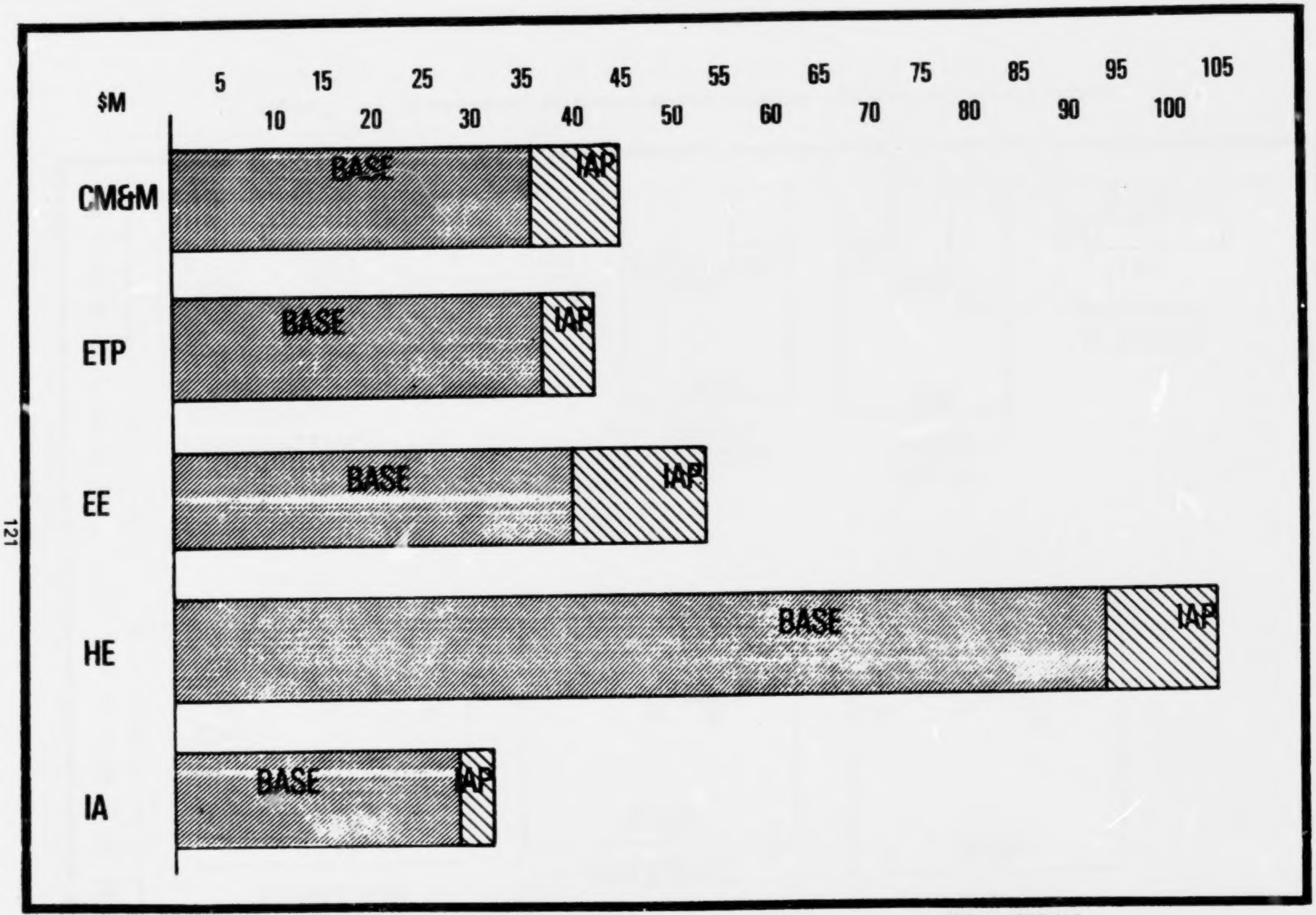


Figure 5. Interagency (pass-thru) energy/environment processes and effects program-funding by major categories (FY-75/76/77).



PROGRAM TOTALS BASE: $236.9M IAP:40.2M TOTAL: 277.1M

Figure 6. Total FY-76 federal funding - energy for related environment and safety biomedical and environmental subcategory.

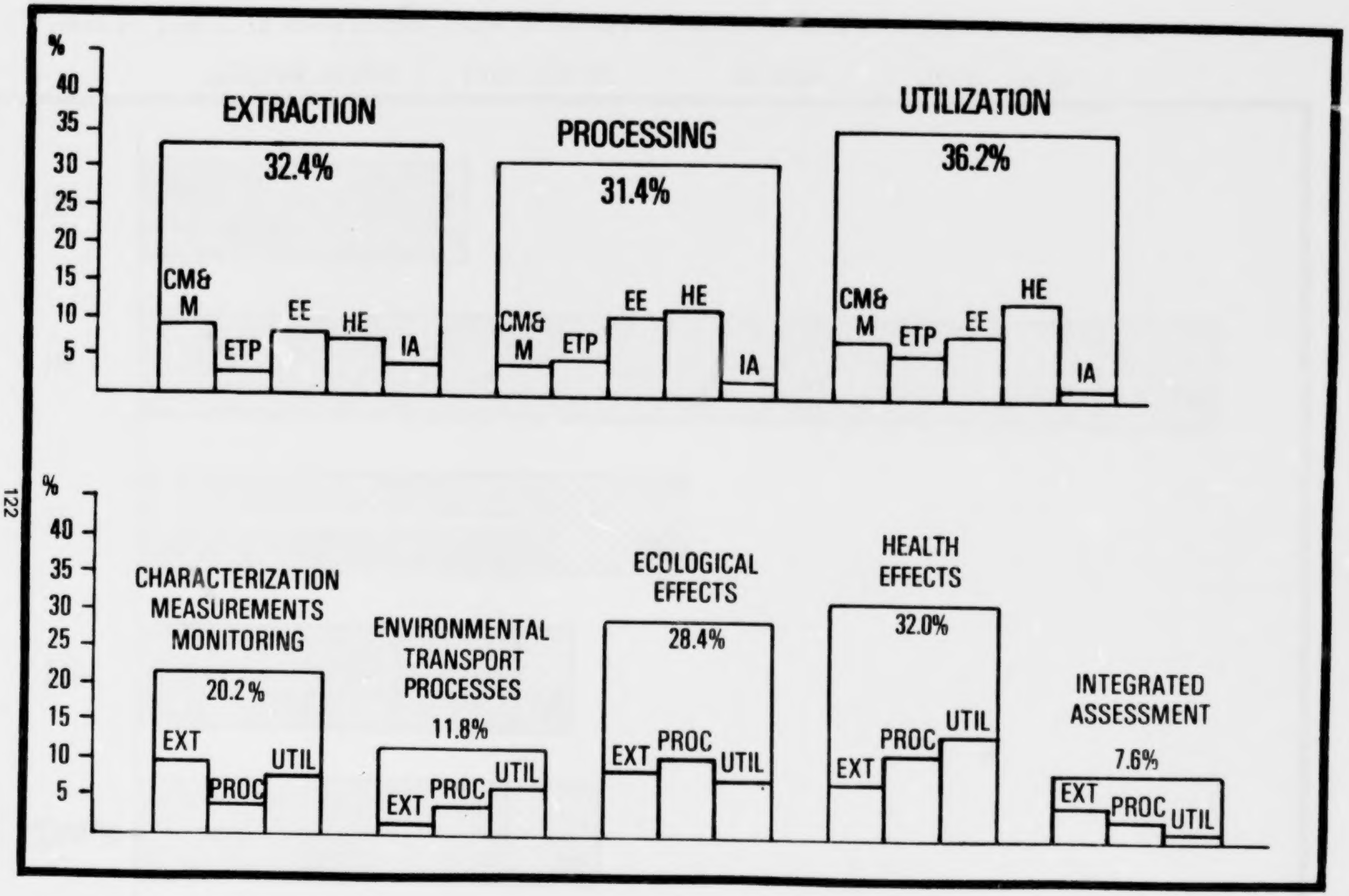


Figure 7. FY-76 interagency (pass-thru) energy/environment program by fuel cycle module.

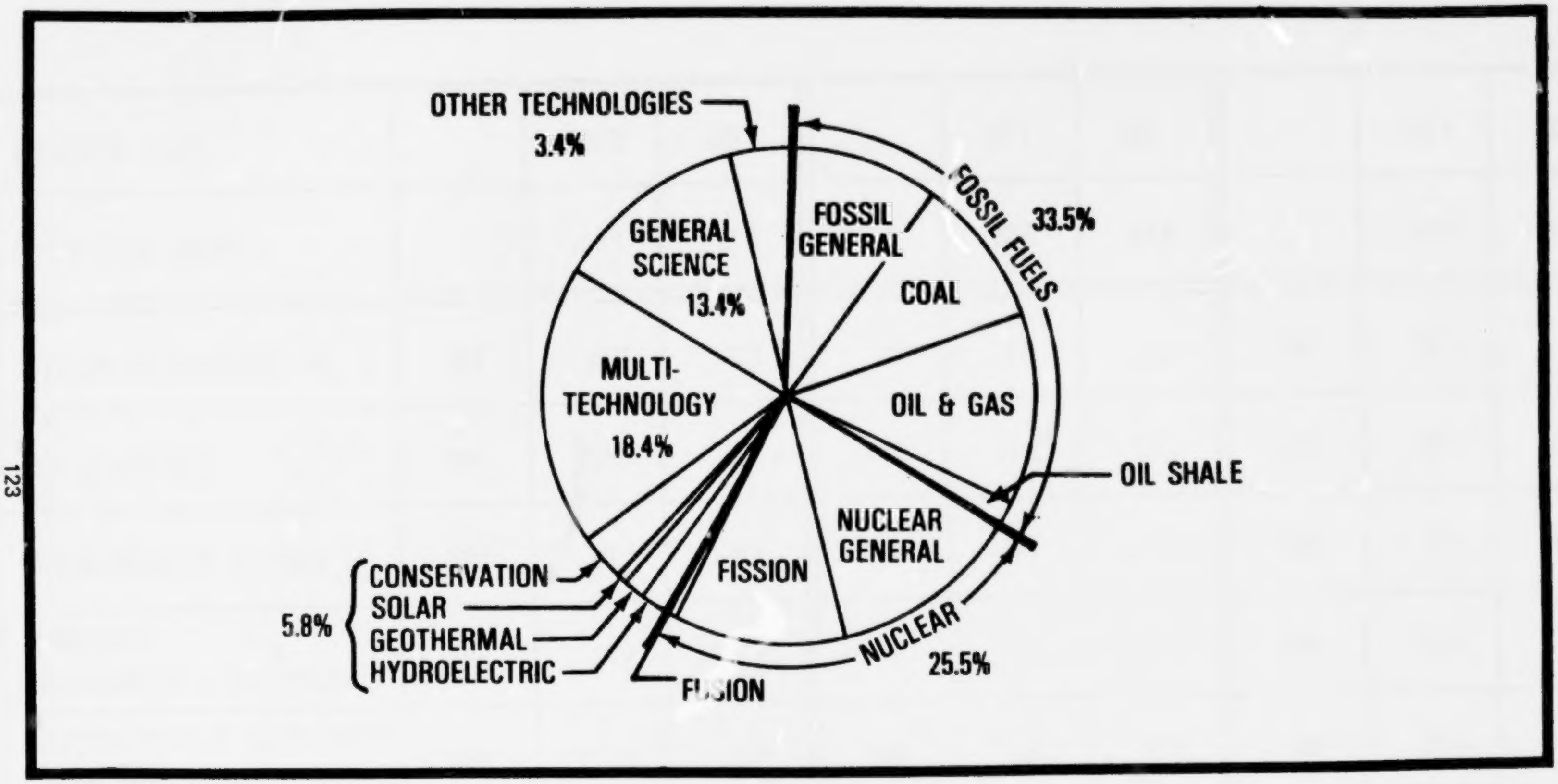


Figure 8. FY-76 base & pass-thru funding for energy/environment program - according to technology.

	BASE			INTERAGENCY PROGRAM (IAP)			TOTAL (ERDA INVENTORY)		
	# OF PROJECTS	$M	%	#	$M	%	#	$M	%
CHARACTERIZATION MEASUREMENT & MONITORING	166	17.4	7.3	129	7.5	18.6	295	24.9	9.0
ENVIRONMENTAL TRANSPORT PROCESSES	289	22.8	9.6	16	4.6	11.4	305	27.4	9.9
ENVIRONMENTAL EFFECTS	236	40	8.2	52	10.8	27.1	288	30.4	11.0
HEALTH EFFECTS	594	29.6	12.4	148	11.4	27.7	742	40.7	14.7
INTEGRATED ASSESSMENT	233	17.3	7.3	14	2.9	7.3	247	20.2	7.3
FOSSIL FUEL TOTAL		106.7	45.8		36.9	92.0		143.6	51.9
PROGRAM TOTAL		236.9	100		40.2	100		277.1	100

Figure 9. FY-76 federal base & pass-thru program - fossil fuel emphasis for each environmental research category.

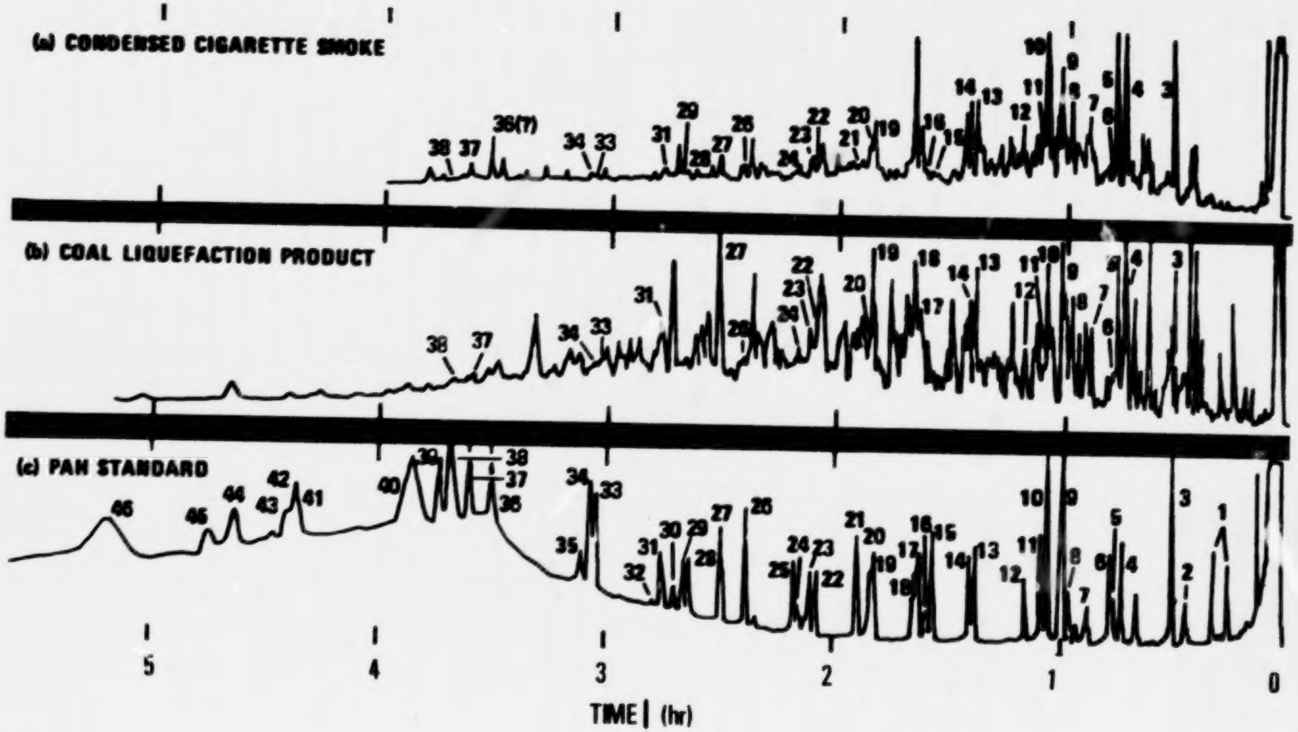


Figure 10. Gas chromatographic profiles of polynuclear aromatic hydrocarbon isolates.

lustrations of the various organic molecules in a chromatogram of condensed cigarette smoke and a polycyclic aromatic hydrocarbon standard are also displayed for purposes of comparison. Several attempts(6,7) have been made to categorize the agents in the waste steams and products. Gehrs, et al.,(6) have suggested that five groups may be sufficient to categorize the organics associated with aqueous wastes as follows:

1. Phenols,
2. Arylamines,
3. Alliphatic Hydrocarbons,
4. Mono and Polycyclic Hydrocarbons, and
5. Sulfur containing compounds (thiophenes and mercaptans).

More detailed listings of the variety of agents known or suspected to be associated with synthetic fuels have been developed. The anticipated adverse biological effectiveness of such agents have also been listed.(7,8,9)

Several recent literature surveys(10,11) suggest that quantitative chemical characterization of the agents in the various products and waste streams associated with each of the several advanced fossil fuel processes is still a major activity. The fractionation, chemical characterization, and bioassay of several products and waste streams have been accomplished. A listing of such materials is presented in Figure 11.

The problem area of characterization, measurement and monitoring has stimulated the following:

1. The development and use of more accurate analytical instrumentation for the quantification of the agents in the waste streams and in the ambient environment;(12,13)
2. The obtaining of baseline information at likely sites;
3. The development of a systematic monitoring meteorology for organic compounds;
4. A procurement of some surrogate standard reference materials.

Surrogate standard reference materials have been developed and distributed by NBS as part of a quality assurance program. The surrogates for polycyclic aromatic hydrocarbons, phenols and for N-heterocyclics have concentrations in the range of 100 ppm in the carrier (water or hexane).

Environmental Transport Processes - A major item of concern with respect to environmental transport processes is the fate of the organics in the various waste streams. Studies have been undertaken to develop models for terrestrial sorption of shale, oil, or aquatic transport and transformation (photo- and bio-) models of the organics in liquid effluents. There does not appear, however, to be an appreciable effort regarding phototransformation of the organics in gaseous waste streams or products.(4,14)

Ecological Effects - In the ecological effects research area, the subjects of major concern specific to synthetic fuels and receiving emphasis include the determination of toxicity of the organics to aquatic species and the bioaccumulation in the food web. Studies undertaken have reflected this concern as indicated by the toxicity studies on zooplankton and various species of fish, using whole effluents and fractions thereof from conversion processes. Bioaccumulation of metals and organics in aquatic species is also under active investigation.(15)

Health Effects - The agents in the products and waste streams associated with synthetic fuel production and use cause an increase in concern for the adverse health effects of carcinogenicity, mutagenicity, and teratogenicity. The health endpoints of behavioral modification, biochemical changes, pathophysiological changes and system dysfunction have also been under investigation. Targets of concern under investigation have ranged from subcellular components to whole animal for a variety of tissues and body fluids. All routes of administration (inhalation, ingestion, injection, and immersion) have been utilized in the experimental studies, but not for all agents of concern, nor for all of the species of interest. Integration of the information obtained from the variety of studies in the various disciplines (bioscreening, animal toxicology, cellular toxicology, clinical and epidemiological studies) to obtain estimates of risk to various population groups represents the most formidable aspect of the health problem, in view of the variety of

- **PRODUCTS**
  - – COED SYNCRUDE PRODUCT OIL
  - – SYNTHOIL
  - – SHALE OIL
  - – SWEET CRUDE
- **AQUEOUS BY-PRODUCTS**
  - – SYNTHANE CONDENSATE
  - – COED SEPARATOR LIQUOR
  - – OIL SHALE RETORT WATER
  - – SOLVENT REFINED COAL PROCESS
- **GASEOUS BY-PRODUCT**
  - – COED STACK GAS

Figure 11. Characterized advanced fossil fuel products and wastes.

scientific opinions regarding the proper interpretation of the data.

As indicated previously, toxicity and mutagenicity evaluations have been undertaken for a number of products and byproducts (aqueous and gaseous). The mutagenicity studies performed by Epler et al.,(16) indicate that all crudes and synfuels show some mutagenic potential, with the relative total varying over two orders of magnitude, and with the mutagenic activities of the natural crudes appearing to be appreciably less than those of the synfuels. The interpretation of these results regarding the hazard to man is still under active investigation, and considerable research is considered necessary before extrapolation is appropriate.

With respect to carcinogenicity, research efforts are addressing the problems of dosimetry at the cellular and organ level, the impact of multiple stressors, the impact of rates of exposure and the development of protocols for retrospective epidemiological studies of occupational population groups. Some investigators are now convinced that a linear non-threshold dose response model is appropriate to use for estimating impacts from primary chemical carcinogens.(17,18)

Integrated Assessment - Most integrated assessments regarding advanced fossil fuel systems suffer from the lack of precise data and require a regular updating.

The first phase of an integrated assessment of energy development in the Western United States(19) confirms the concern that such development may well produce regional as well as local air pollution problems. This study has cast doubt on the need for large quantities of water for synfuel production.

Integrated assessments are also underway for other regions (Southeast, Pacific Northwest, Ohio River Basin) as well as on a national (i.e., electric utility ITA, National coal utilization assessment) or local scale.

Some Problems

As indicated previously, a major problem that exists is the lack of precise data that is useful for integrated assessments. Part of this problem stems from the lack of sufficient understanding of the most appropriate indicators to use for the assessment. This lack of understanding is reflected in the quantity and variety of data that are being obtained at great expense, in some cases, but of relatively little value. There appears to be a lack of integration of the data on a regular basis for each of the major items of concern. Some estimate of the uncertainties associated with the assessments should be made on a regular basis to assist planning of future research necessary to reduce the uncertainties.

In the health effects area, a major problem is the procurement of sufficiently large quantities of well-characterized pollutants, products, and environmentally transformed materials to engage in statistically valid in vivo experiments. Some efforts are underway to develop a repository at Oak Ridge National Laboratory under an interagency agreement between EPA and ERDA. Cooperation from all of those engaged in developing energy technologies will be necessary in order for the repository to function in a useful manner on a time scale compatible with the developing techniques.

An additional item of major concern is the lack of information pertaining to the modification of the spectrum of agents that are released, that occurs as a consequence of scaling up of processes and control systems. The developers of the processes and technologies consistently argue that the spectrum of agents from a full-scale commercial facility will be vastly different than those from a model.

Those engaged in health and ecological effects research could be more helpful to the designers of energy and control systems if a cooperative attack on the problem was utilized during the early stages of development.

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FIGURES

1. OMB-CEQ WORKING GROUPS ON ENERGY-RELATED ENVIRONMENTAL RESEACH.
2. INTERAGENCY PLANNING STRUCTURE.
3. ENVIRONMENTAL PATHWAYS MODEL.
4. RELATIONSHIPS AMONGST HEALTH RESEARCH SUBCATEGORIES.
5. INTERAGENCY (PASS-THRU) ENERGY/ENVIRONMENT PROCESSES AND EFFECTS PROGRAM-FUNDING BY MAJOR CATEGORIES. (FY-75/76/77)
6. TOTAL FY-76 FEDERAL FUNDING -ENERGY FOR RELATED ENVIRONMENT AND SAFETY BIOMEDICAL AND ENVIRONMENTAL SUBCATEGORY.
7. FY-76 INTERAGENCY (PASS-THRU) ENERGY/ENVIRONMENT PROGRAM BY FUEL CYCLE MODULE.
8. FY-76 BASE & PASS-THRU FUNDING FOR ENERGY/ENVIRONMENT PROGRAM - ACCORDING TO TECHNOLOGY.
9. FY-76 FEDERAL BASE & PASS-THRU PROGRAM - FOSSIL FUEL EMPHASIS FOR EACH ENVIRONMENTAL RESEARCH CATEGORY.
10. GAS CHROMATOGRAPHIC PROFILES OF POLYNUCLEAR AROMATIC HYDROCARBON ISOLATES.
11. CHARACTERIZED ADVANCED FOSSIL FUEL PRODUCTS AND WASTES.

Session II: **ENVIRONMENTAL ASSESSMENT**

E. C. Cavanaugh
Chairman

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LOW-BTU GASIFICATION-ENVIRONMENTAL ASSESSMENT

William E. Corbett
Radian Corporation
8500 Shoal Creek Boulevard
Austin, Texas 78758

Abstract

Radian Corporation is under a 3-year contract to EPA's Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina, to perform a comprehensive environmental assessment of low-Btu gasification and its utilization. The period of this contract is March 1976 through March 1979. In this paper, the scope and current status of Radian's effort on this program as well as a general summary of the results achieved to date are presented.

Basically, Radian's technical activities have fallen into three general task areas: environmental assessment, data acquisition and program support. To date, the bulk of the program effort has been expended in compiling and assessing current data on low-Btu gasification process technology and its related environmental impacts. As part of this effort, a data base containing over 10,000 articles and contact reports has been compiled and assessed.

Concurrently, a significant effort has been directed toward making arrangements for conducting environmental tests at operating gasification plants both in this country and abroad. The candidate commercial test sites being considerd in this country are all equipped with fixed-bed, air-blown, atmospheric pressure gasifiers. Efforts to expand the range of gasifiers and coal types tested have led to a consideration of ERDA-sponsored as well as overseas facilities as candidate test sites. While final arrangements for site testing activities are not yet complete, future program effort is expected to be concentrated in the area of acquiring and analyzing environmental test data.

INTRODUCTION

This paper is based upon information compiled in an ongoing EPA program whose objective is a comprehensive environmental assessment of low/medium-Btu gasification and utilization technology. This three-year assessment program was initiated in March 1976. Radian's program efforts are therefore about half complete at this point.

One of the first questions that one faces when dealing with a very broad subject area such as environmental assessment is: "What is an environmental assessment?" Since this subject is covered in detail by Bob Hangebrauck in another paper, I will not dwell on this issue. However, I would like to reiterate some of the key elements of EPA's overall approach to environmental assessment since this will provide some very important background information on Radian's program efforts.

ENVIRONMENTAL ASSESSMENT PROGRAM GUIDELINES

Basically, EPA's overall environmental assessment program objectives, as defined by Hangebrauck[1] are:

1. to determine the multimedia environmental loadings and costs associated with the application of alternative control methods to potential low/medium-Btu coal gasification plant emission sources; and
2. to compare the magnitudes of those projected loadings with appropriate target values established through surveys of existing regulations, estimates of multimedia environmental goals or the results of bioassay screening tests.

Ultimately, this effort should result in a specification of:

1. potential emission sources of environmental concern in a coal gasification facility;
2. the effectiveness and cost of controlling those emissions to varying levels through the application of candidate control methods; and
3. areas in which existing controls appear to be inadequate for purposes of controlling hazardous pollutant emissions to acceptable levels.

Development needs identified as a result of this effort will be expressed such that control

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technology development priorities are clearly indicated.

The specific tasks which have been defined by the EPA as being necessary to complete an environmental assessment are the following:

1. Current Process Technology Background;
2. Environmental Data Acquisition;
3. Current Environmental Background;
4. Environmental Objectives Development;
5. Control Technology Assessment; and
6. Environmental Alternatives Analysis.

The general types of activities which will take place in each of these task areas are fairly obvious from the task titles. For a more detailed description of these tasks, the reader should refer to the previously referenced Hangebrauck document[1].

Radian's program activities to date have been concentrated in the first two of the six task areas listed above. Our first iteration at assessing the current status of and significant trends in low/medium-Btu gasification and utilization technology was marked by the release of a draft document by Cavanaugh, et al., June 1977[2]. Significant effort has also been devoted toward making arrangements for conducting environmental tests at pilot and commercial scale gasifiers located both in this country and abroad. At the present time, one major testing campaign has been completed at an existing commercial U.S. site and several other tests are planned.

Because the bulk of our program progress has been made on the Current Process Technology Background and the Environmental Data Acquisition tasks, this paper will concentrate on the results of our efforts in these two task areas. While our work in the other task areas has started, to date these efforts have mainly taken the form of working in conjunction with the EPA and other prime contractors to establish methodologies and examples of useful outputs from these tasks.

More specifically, this paper will concentrate on the following aspects of Radian's environmental assessment program. First, the environmental data base which we have accumulated to date on low/medium-Btu gasification technology will be summarized. As part of this discussion, the resources used to compile this data base, the environmental problem areas identified and the driving forces which appear to be controlling the commercialization of the technology will be described. This discussion will naturally lead to a discussion of the guidelines we have used in formulating priorities for our environmental data acquisition program. Finally, I will describe the test site opportunities we have identified and our overall strategy and timetable for conducting meaningful environmental tests.

CURRENT PROCESS TECHNOLOGY BACKGROUND

The approach which we have taken in trying to gain an insight into the current status of low/medium-Btu gasification technology has involved an aggressive campaign to procure available information from two major sources:

1. the open literature; and
2. contacts with experts.

Obtaining information from the first of these two resource areas involved an extensive literature survey utilizing both computer-aided and manual search techniques. Abstracts of publications relating to all aspects of this program were systematically screened, catalogued and cross-referenced using keywords established by project personnel. To facilitate this effort, a special project library was set up to support the activities of the technical members of the project team. To date, a gasification process environmental data base containing over 10,000 articles, news releases and contact reports has been systematically compiled as a result of this effort. The approach used in setting up this information handling system is documented in an interim project technical report.[3]

Although the open literature has provided a considerable amount of useful information on this program, efforts to establish a dialogue with persons who have active interests in gasification technology application and development have been far more fruitful in helping our project team to develop a meaningful perspective of current trends. This effort has also helped considerably in the area of identifying candidate sites for environmental testing. This aspect of the project will be summarized in a later section of this paper.

Modular Approach

One of the major problems which was faced on this program was related to the question of how you represent a very complex technology composed of a large number of candidate processes which can be arranged in many different ways. In its most simplified form, low/medium-Btu gasification technology can be represented by the following block diagram

COAL
GASIFICATION TECHNOLOGY
GASEOUS FUEL

but, this approach does not provide a very meaningful mechanism for organizing and interpreting process and control technology information. One approach to this problem of analyzing a complex technology which has proven itself to be useful in several previous EPA programs is a modular or unit operations approach.

With this approach, a complex technology or industry is broken down into its generic unit operations, each of which is characterized as having specific input and output streams. On this basis, the production of low/medium-Btu gas can be assumed to require the process operations shown in Figure 1. Each of these unit operations can in turn be represented by a series of optional process modules as shown in Figures 2, 3 and 4.

Now, while a technology can be represented in a general sense by block diagrams such as those shown in Figures 1-4, site-specific environmental determinations must be based upon an analysis of a specific coal feed which is converted into a product which is consumed by a specific end user. For this reason, it is important to consider the potential end uses of low/medium-Btu gas as well as the specific processes which appear to be best suited to producing the required product gas.

Significant End Use Options for Low/Medium-Btu Gas

Potential end uses for low/medium-Btu gas which apear to be commercially significant at present are:

1. as a fuel for direct firing of process heaters requiring a clean fuel gas. This is a very likely near-term application for the technology;
2. as a fuel for process heaters and steam boilers which cannot economically be converted to direct coal-fired units. This option is most attractive in a situation where a gasification system can be used to supply large number of remote users;
3. as a gas turbine fuel, including use in combined cycle units. One potentially attractive approach here is the use of a gasifier and storage system to supply fuel for a utility peaking turbine; and
4. as a synthesis or reducing gas. This end use option would not be competitive with liquid fuel reforming in most applications.

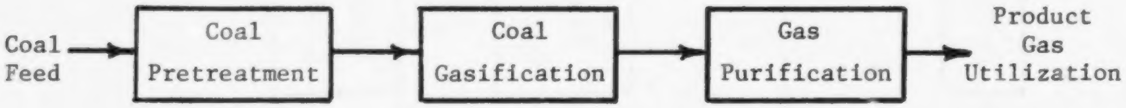

Figure 1. Coal gasification process unit operations.

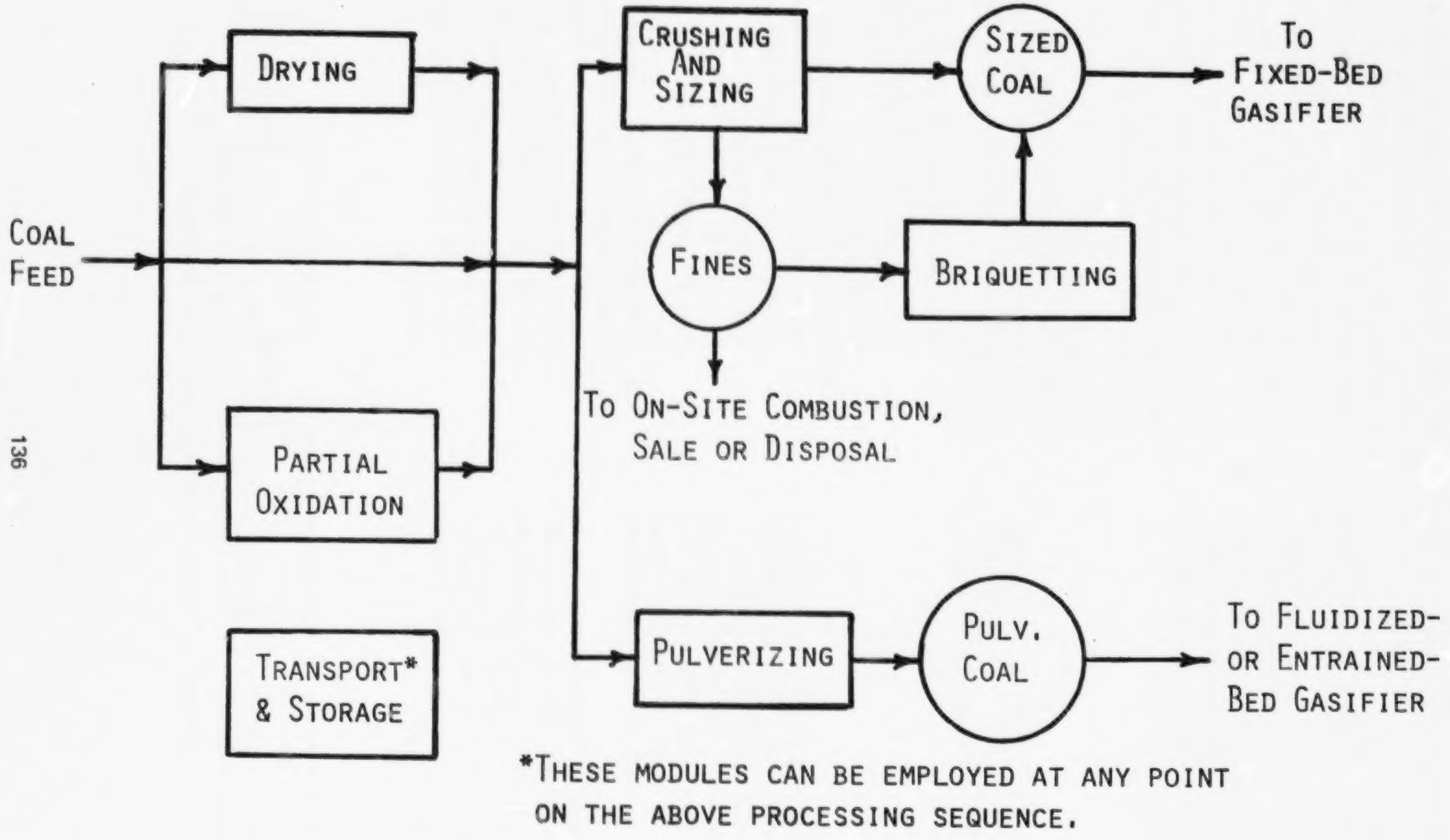
Coal Feed
Drying
Partial Oxidation
Transport* & Storage
Crushing And Sizing
Fines
To On-Site Combustion, Sale or Disposal
Sized Coal
Briquetting
To Fixed-Bed Gasifier
Pulverizing
Pulv. Coal
To Fluidized- or Entrained-Bed Gasifier
*These modules can be employed at any point on the above processing sequence.

Figure 2. Process modules—coal pretreatment operation.

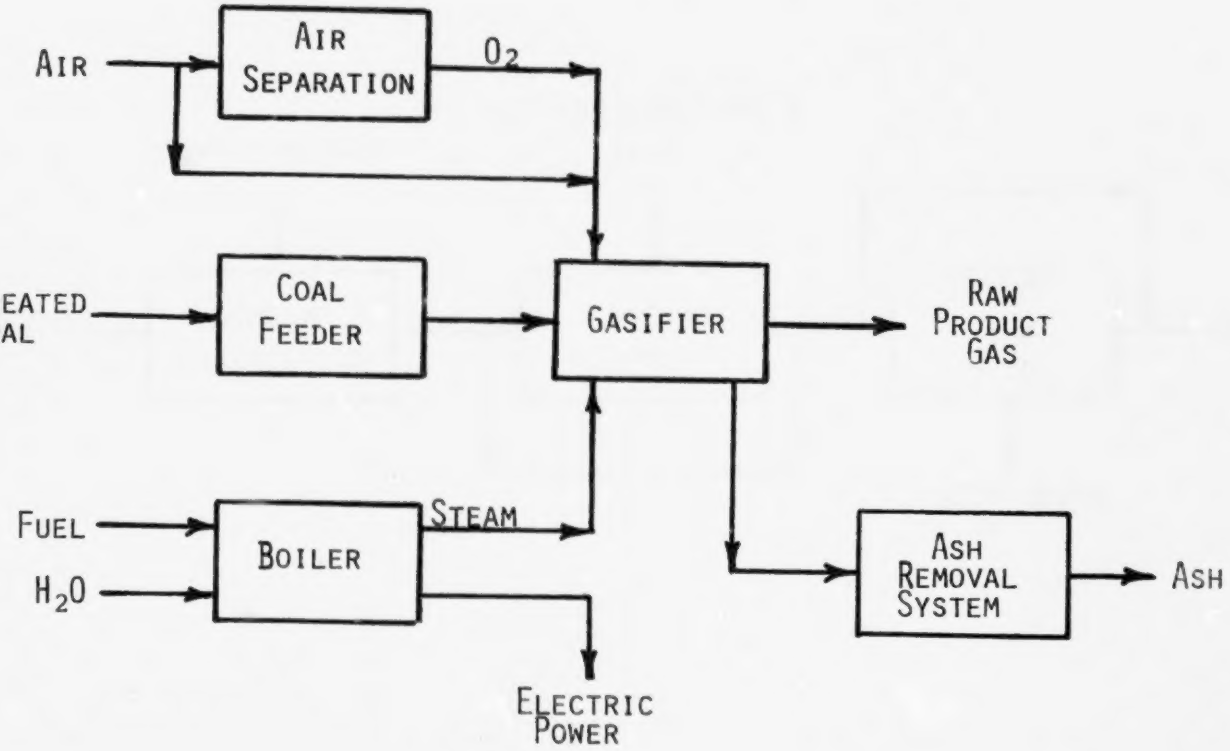
AIR
AIR SEPARATION
O_2
PRETREATED COAL
COAL FEEDER
GASIFIER
RAW PRODUCT GAS
FUEL
H_2O
BOILER
STEAM
ELECTRIC POWER
ASH REMOVAL SYSTEM
ASH

Figure 3. Process modules—coal gasification operation.

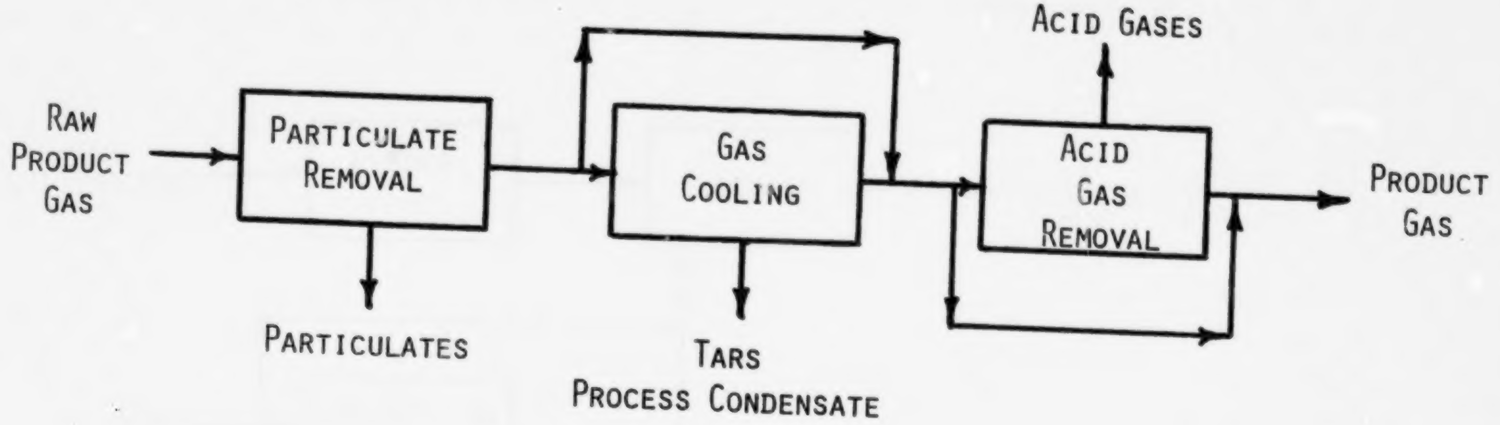
Raw Product Gas
Particulate Removal
Particulates
Gas Cooling
Tars
Process Condensate
Acid Gases
Acid Gas Removal
Product Gas

Figure 4. Process modules—gas purification operation.

All of these end uses for clean gaseous fuels have traditionally been satisfied by natural gas consumption. As this country's natural gas supplies diminish, however, many industrial users of natural gas are finding that low/medium-Btu gas is becoming an increasingly attractive alternative to the complete replacement of existing gas-fired facilities.

Significant Processing Options

The gasification processes that appear to be best suited to satisfying near-term needs for low/medium-Btu gas are listed in Table 1. While this is by no means a complete list of available processes, it does include most of the systems for which there appears to be considerable commercial or governmental agency support.

TABLE 1

PROMISING LOW/MEDIUM-BTU GASIFICATION SYSTEMS

Commercial Widespread Use	Commercial Limited Use	Developmental
Koppers-Totzek	Chapman (Wilputte)	Bi-Gas
Lurgi	Riley Morgan	BGC Slagging Lurgi
Wellman-Galusha		Foster Wheeler/Stoic
Winkler		GFERC Slagging
Woodall-Duckham/Gas Integrale		MERC Pressurized Wellman-Galusha
		Texaco

As shown in Table 2, these promising gasification systems fall into six different groups when classified on the basis of their significant design features. This classification scheme is also significant from an environmental standpoint because the product, by-product and emission streams associated with these various gasifiers will vary considerably as functions of the process design features listed.

For example, relative to high temperature, entrained-bed systems, fixed-bed systems will tend to produce a product gas that contains significantly greater quantities of coal devolatilization products. This will create more of a tar/oil fraction handling and disposal problem. Relative to dry ash systems, slagging systems will produce a fused ash material

TABLE 2

PROMISING LOW/MEDIUM-BTU GASIFICATION SYSTEMS

Classification By Gasifier Type			
Fixed Bed	Dry Ash	Atmospheric	Chapman (Wilputte)
			Foster Wheeler/Stoic
			Riley Morgan
			Wellman-Galusha
			Woodall Duckham/GI
		Pressurized	Lurgi
			MERC
	Slagging	Pressurized	BGC Lurgi
			GFERC
Entrained Bed	Slagging	Atmospheric	Koppers-Totzek
		Pressurized	Bi-Gas
			Texaco
Fluid Bed	Dry Ash	Atmospheric	Winkler

which should exhibit significantly different leaching characteristics.

The requirements of the coal pretreatment module are generally dictated by the properties of the feed coal and the feed specifications of the gasifier used. Gas purification process requirements are determined by the specifications of the intended end use process. Again, these process constraints are environmentally significant. Potential emissions of volatile organics from coal drying and partial oxidation processes appear to be a troublesome problem. By the same token, gas cooling and low temperature acid gas removal processes generate a tar/oil stream and a process condensate which are difficult to dispose of in an environmentally sound manner. Applications which can utilize hot, raw gasifier product gas directly can avoid this troublesome problem, a consideration which explains one of the main driving forces behind efforts to develop high temperature acid gas removal processes.

A factor which is not addressed in this paper, but one which must be kept in mind, is that process economics will ultimately dictate the choice of a coal feedstock, process configuration and process operating conditions for a given application. This choice must take into account the environmental tradeoffs and control technology requirements associated with various process options, but, in the final analysis, process and control technology options will both be selected on an economic basis.

Environmental Problem Areas

In addition to providing a more detailed breakdown of the modules required to satisfy the requirements of the three major process operations, Figures 2, 3, and 4 also provide a useful starting point for the identification of potential gasification plant environmental problem areas. In the coal pretreatment operation, there are three major classes of emission problems:

1. coal dust emissions from all coal handling and storage operations;
2. volatile component emissions from all modules that involve the thermal treatment of coal (drying, partial oxidation and possibly briquetting and storage); and
3. water runoff from coal storage areas or from the use of water sprays for dust suppression.

Qualitatively, the coal dust emitted from coal handling operations would be similar to the coal feed material, but good techniques for calculating dust emission rates as functions of coal properties and the characteristics of the process hardware are not available. Some data on coal devolatilization products have been reported, but much of this information is of limited use to this program. The leaching characteristics of a variety of specific coal types are probably better defined than some of these other problem areas, but additional work on specific coals which appear to be reasonable candidates for gasification process feed materials is needed.

In the coal gasification operation the major sources of environmental emissions are:

1. gasifier start-up vent;
2. leaks and other fugitive emissions of raw product gas, e.g., through the coal feeding device;
3. ash handling procedures which can generate ash dust; and
4. leached ash components (associated with rainfall or ash sluice water) which are a problem in wet ash handling systems.

The gasifier start-up vent stream would normally be flared. One question related to this operation for which no data exist is, "Are hazardous raw gas components adequately controlled using this approach?" This question of hazardous component behavior in combustion processes is a much broader issue, however. The fate of both tar and low/medium-Btu gas components in combustion processes warrants considerable further study since this issue impacts:

1. the emissions of hazardous components from many candidate product/by-product utilization processes; and
2. the adequacy of incineration or flaring as a control technique for hazardous hydrocarbon vapors.

In the gas purification operation, the major sources of emission streams are:

1. particulate removal processes which remove tar aerosols and coal fines from the hot raw product gas;

2. quenching operations which usually produce condensed organic (tar/oil) and aqueous (process condensate) materials. Disposal or treatment of these materials is a very troublesome problem because of the wide range of pollutants they contain;
3. acid gases removed from the product gas; and
4. fugitive emissions from handling all of these materials.

As a general statement, it can be said that a significant amount of data are available on environmental problems associated with coal gasifier operations. These data are inadequate for purposes of making comprehensive environmental and control technology assessments, however. Of particular importance to this program are data which

- provide more detailed characterizations of the types of emissions streams just discussed,
- specify levels of hazardous components present in those streams as functions of key process variables, and
- predict the fates of those components in utilization and/or treatment processes.

It is these objectives which are now guiding our current efforts to expand our environmental data base through meaningful test programs at operating gasification sites.

ENVIRONMENTAL DATA ACQUISTION

In this section, the concerns which are guiding Radian's overall data acquisition effort are described. Our current approach to conducting environmental tests at a specific site is summarized in a paper by Bombaugh[4], so this issue will not be addressed here.

Sites which were considered to be potential candidates for environmental testing include:

- domestic facilities
  - operating commercial-scale units
  - developmental/demonstration units
- foreign facilities
  - a wide range of commercial-scale test opportunities is represented by this group.

Commercial scale gasifiers which are presently operating in this country are shown in Table 3. Of this group, only the Holston gasifier has been tested to date. Environmental testing of a Wellman-Galusha gasifier at Glen-Gery's York, Pennsylvania plant is planned for early 1978 in conjunction with ERDA's industrial gasifier test program. No firm plans exist for conducting tests at the other two sites listed, although extensive discussions of test possibilities have been held with the two groups involved.

Several limitations in the test possibilities afforded by these commercial gasifiers are obvious from the data presented in Table 3. All of these sites use fixed-bed, air-blown gasifiers. The only particulate removal technique utilized is a hot cyclone. Only one site has gas quenching and tar/condensate handling facilities. Only one gasifier uses a variety of coal types.

Because of these limitations in commercial sector test opportunities, consideration of alternate domestic sites for environmental testing is justified. Some of the possibilities here are

- EPA-sponsored test units at Research Triangle Institute and North Carolina State University which will study gasification process pollutant generation and control technology effectiveness,
- ERDA-sponsored development units at MERC and GFERC,
- ERDA-funded gasifiers which will be installed at a variety of domestic sites, and
- privately-funded development units.

The EPA-sponsored test units are not yet operational. Discussions have been held with MERC and GFERC representatives concerning possibilities for cooperative EPA/ERDA test programs, but no specific agreements have been reached. The first ERDA-sponsored industrial gasifier to be started up will be Glen-Gery's York, Pennsylvania unit. The next gasifier is not scheduled for startup until at least the third quarter of 1978. Discussions with a large number of private sponsors of gasification-related R&D programs have been held, but, to date, no promising test opportunities in that area have been identified.

Because of this further limitation in the

TABLE 3

CANDIDATE DOMESTIC TEST SITES-OPERATING COMMERCIAL GASIFIERS (ALL LOW-BTU)

Site	Gasifier and Coal Type	Cleanup	Utilization
Holston Army Ammunition Plant Holston, TN.	Chapman Bituminous	Hot Cyclone Water Quench Two Stages of Water Scrubbing	Low-Btu Gas-Burned in Process Furnace Tar-Burned in Boiler
Glen-Gery Brick Co. 4 Sites in Eastern PA.	Wellman-Galusha Anthracite	Hot Cyclone	Gas Burned in Brick Kiln
National Lime Carey, Ohio	Wellman-Galusha Bituminous	Hot Cyclone	Gas Burned in a Lime Kiln
Riley Stoker Demonstration Unit Worcester, MA.	Riley-Morgan Variable	Hot Cyclone	Gas Flared

availability of viable developmental sites in this country, a number of commercial sites in foreign countries have been considered as candidates for environmental testing. Process and emission data will be obtained from a medium-Btu gasification facility located in Kosovo, Yugoslavia starting in the fall of this year. Details of this program are described in a paper by Mitrovic[5]. The possibility of conducting environmental tests in Europe and Africa is being jointly pursued by Radian and TRW, but, to date, no firm developments in this area can be reported.

SUMMARY AND CONCLUSIONS

The conclusions which can be drawn from the results of Radian's program efforts to date fall into three general areas:

- Current Technology Status
- Need for Environmental Data Acquisition
- Test Opportunities

On the subject of the current status of low/medium-Btu gasification, there is very clearly a significant interest in the near-term application of this technology in the United States. The most promising potential market appears to be associated with supplying the gaseous fuel needs of existing industrial processes which can no longer depend upon traditional sources of natural gas. Use of low/medium-Btu gas as a gas turbine fuel or as a synthesis/reducing gas may be feasible in some applications, but widespread usage of gasification technology to satisfy these demands is not anticipated to be significant in the near term.

Radian's survey of available data on the environmental aspects of low/medium-Btu gasification processes has shown that existing data are not sufficient to support the level of analysis required to produce the desired end products of this assessment program. Major deficiencies are found in the areas of characterizing the emissions of minor and trace contaminants from gasification processes (particularly trace organics). There is also a general lack of information on fugitive emissions and minor process vent streams.

Available U.S. test sites will provide opportunities for gathering useful environmental data on fixed-bed, atmospheric pressure systems using anthracite and bituminous coal feedstocks. Efforts to expand the range of gasifiers and coal types available for testing has led us to push for involvement in both ERDA-sponsored and overseas test programs. Radian participation in these programs will be a key element in the development of an ability to predict the impact of coal feedstock and process variable changes upon control technology needs.

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HIGH BTU GASIFICATION ENVIRONMENTAL ASSESSMENT - WORK STATUS AND PLANS

Charles F. Murray, Program Manager
Masood Ghassemi, Senior Project Engineer

Environmental Engineering Division
Energy Systems Group of TRW, Inc.
Redondo Beach, California 90278

Abstract

This recently initiated 3-year study is aimed at environmental assessment of high-Btu coal gasification including identification of the control technology needs for the industry. The effort consists of: (a) evaluation of existing process and environmental data and the data which are being generated by other EPA/ERDA contractors working in related areas; (b) acquisition of supplementary data through sampling and analysis of process/waste streams at selected gasification facilities; and (c) environmental assessment and necessary process engineering support studies.

The program activities fall into three work areas: Environmental Assessment, (Field) Data Acquisition, and General Program Support. The work areas are broken down into a total of 17 interrelated tasks. To provide program flexibility, a "work package" approach is used by EPA to authorize work relevant to specific tasks in the program. A total of nine Technical Directives have been issued by EPA authorizing work relevant to 10 tasks.

Most of the effort in the program to date has been in connection with two technical directives, Acquisition and Analysis of the Data Base, and Site Locations and Information. A large number of pertinent background documents have been acquired. Nine gasification processes have been selected for detailed analysis. A "modular" approach has been chosen for analysis and presentation of data on gasification, gas treatment, pollution control, and integrated facilities. Draft "gasification data sheets" have been prepared for six of the nine processes considered. Preliminary discussions have been held with ERDA and a number of private process developers to enlist their cooperation in identifying potential sites for environmental sampling and in arranging for such sampling.

INTRODUCTION

Under a contract awarded to TRW in May 1977 by EPA/IERL-RTP, TRW is currently working on a 3-year program to (a) characterize the waste streams associated with the operation of commercial high-Btu gasification facilities using current and developmental conversion technologies, (b) identify the control technology required to reduce or eliminate waste discharges, and (c) estimate the environmental impacts at selected sites. The study will provide input to the EPA effort for developing and demonstrating control technologies for emerging industries and for establishing the technical basis for drafting new source performance standards for gasification plants.

Because the program has only been started very recently, sufficient results are not available for presentation at this time. This paper will present a description of the program in terms of its structure and the mechanism by which tasks in the program are initiated. The objectives of and the preliminary accomplishments in the few tasks that have been initiated will also be reviewed.

GENERAL STUDY APPROACH AND WORK BREAKDOWN STRUCTURE

The technical approach for achieving the program objectives consists of the following activities:

1. Generation of a gasification/gas upgrading, control technology, and impact assessment baseline.
2. Definition of information gaps and deficiencies and areas for productive application of engineering analysis.
3. Conduct of field sampling and analysis programs aimed at filling data gaps and providing needed information.
4. Conduct of selected engineering analyses to supplement available process and control equipment information.

5. Integration of all information and data into assessment and technology overview documents.

For planning purposes and to provide for effective program management, the program has been divided into three work areas: Work Area A, Environmental Assessment; Work Area B, Data Acquisitions; and Work Area C, General Program Support. A brief description of the activities in and the specific objectives of each work area follows.

Work Area A - Environmental Assessment

The overall objective of Work Area A is to assess the environmental impacts associated with commercial-scale high-Btu gasification operations. The environmental assessment will be based upon (a) review of the published literature on gasification processes and related control technologies; (b) data which are being generated by other EPA contractors working in related areas (e.g., low/medium Btu gasification environmental assessment; coal liquefaction environmental assessment, etc.); (c) data to be acquired from process developers and government agencies; and (d) data to be generated in Work Area B through environmental sampling at high-Btu gasification sites, in Work Area A through process engineering, and in Work Area C through support studies. More specifically, the efforts in and the objectives of Work Area A are as follows:

- Evaluation of available data relative to gasification, gas processing technology and economics, input material characteristics, current control technologies, and process/equipment environmental characteristics.
- Preparation of a technology overview document.
- Prioritization, in order of projected commercial viability, of gasification processes.
- Identification and prioritization of emissions data and information gaps.
- Evaluation of the potential of developmental control technologies.
- Process engineering studies to aid in evaluation of data validity; resolution of data conflicts and filling data gaps.
- Integration of the Work Area B data into technology overview and impact assessment documents.
- Projection, on a common production basis, of the impact data base to commercial scale.

To accomplish the above-listed objectives, and for planning purposes, Work Area A has been subdivided into a total of nine interrelated tasks. A listing and brief description of these tasks are presented in Table 1.

Work Area B - Data Acquisitions

To be meaningful and technically valid, the environmental assessment of high Btu gasification should be based, as far as practicable, on actual process and emissions data for existing commercial and pilot plant facilities. Since only a limited amount of such data is currently available, in the present program considerable emphasis is placed on data acquisitions through comprehensive environmental sampling and analysis at selected pilot plant/commercial facilities. Reflecting this emphasis and for planning purposes, about 40 percent of the program funds and manpower has been earmarked for data acquisitions. The sampling and analysis program will be aimed primarily at generating data to fill some of the gaps identified in Work Area A. More specifically, Work Area B involves the following activities/objectives:

- Identification of representative candidate high-Btu gasification process, gas cleaning and upgrading sampling sites, and assessment of the likelihood of gaining access to these sites for sampling purposes.
- Ranking of candidate sites, based upon operator cooperation, process stage of development, and other factors.
- Organization, cost and planning of the field and laboratory sampling, and analysis efforts associated with each selected site.
- Implementation of field and laboratory data acquisition programs at the selected sites.

To accomplish the above listed objectives in an orderly manner, Work Area B has been sub-

TABLE 1

WORK AREA A TASK DESCRIPTIONS

Task	Description
A1 - Technology Overviews	Overview report on status and technical/environmental aspects of gasification processes.
A2 - Impact Assessments	Preliminary impact assessments to identify data needs.
A3 - Input Material Characterizations	Review of physical/chemical characteristics of process input materials.
A4 - Process Engineering	Material/energy balances and other engineering analyses to characterize integrated facilities, resolve data conflicts and verify data accuracy.
A5 - Control Technology Evaluation	Review of pollution control technologies applicable to gasification.
A6 - Accidental and Transient Pollutant Releases	Identification of potential sources and nature and quantities of pollutant emissions during accidents and transient operations.
A7 - New Control Technology	Conceptual designs of applicable new control technologies and in-plant changes, and/or modifications of existing control technologies.
A8 - Revised Impact Assessments	Detailed environmental assessment incorporating the data generated in the program.
A9 - Revised Technology Overviews	Updated technology overviews, incorporating additional data and findings.

divided into a total of six tasks as described in Table 2.

Work Area C - General Program Support

Major activities in Work Area C include: (a) collection and maintenance of background data on the technology and environmental aspects of high-Btu gasification including preparation and periodic updating of an "analysis of the data base" document; (b) performance of miscellaneous document reviews, surveys and special studies on an as required basis to support program activities in Work Areas A and B; and (c) providing program management and control functions, including reporting to EPA and coordination with other EPA contractors working in related areas. For planning purposes, Work Area C has been subdivided into three tasks described in Table 3.

Work Authorization Via Technical Directives

To provide maximum program flexibility and to accommodate changes in program emphasis which may become necessary as the program proceeds, a "work package" approach is used by EPA to authorize work in a specific task or elements of one or more tasks. The scope of the effort in each work package, the funding level and the performance period are specified in work authorization "Technical Directives" (TD's) which are issued by the EPA Project Officer. To date, a total of nine TD's have been received authorizing work relevant to Tasks 1 through 5 in Work Area A; Tasks 1 and 2 in Work Area B; and Tasks 1, 2, and 3 in Work Area C (see Tables 1, 2, and 3 for task descriptions.) These TD's, the relevant tasks covered, the TD issue dates, and performance periods are listed in Table 4.

TABLE 2

WORK AREA B TASK DESCRIPTIONS

Task	Description
B1 - Site Locations and Information	Identification of potential domestic and foreign test sites and establishment of initial contacts.
B2 - Data Possibilities	Test site screening and prioritization and identification of sampling opportunities.
B3 - Test Program Development	Preparation of detailed sampling plan for Level 1 environmental assessment for selected sites.
B4 - Cost Estimates	Estimation of sampling/analysis costs.
B5 - Testing	Field testing and laboratory analyses.
B6 - Data Analysis and Reporting	Reduction and evaluation of the test data.

TABLE 3

WORK AREA C TASK DESCRIPTIONS

Task	Description
C1 - Background and Evaluations	Collection and evaluation of background engineering/environmental data, and identification of data gaps and conflicts; special studies/surveys in support of program activities.
C2 - Reporting and Coordination	Preparation of reports and coordination with EPA, EPA contractors and other agencies.
C3 - Program Management	Program management including financial control.

TABLE 4

TECHNICAL DIRECTIVES, RELEVANT TASKS, ISSUE DATES, AND PERFORMANCE PERIODS

TD #	Title	Relevant Task(s)*	Date Issued	Performance Period
001	Work Plan Preparation and Coordination	C-2	5-3-77	5 mo.
002	Acquisition and Analysis of the Data Base	C-1	6-22-77	6 mo.
003	Technology Overview Process Engineering	A-1 A-4	6-22-77	6 mo.
004	Site Locations and Information	B-1	6-22-77	7 mo.
005	Program Management, Coordination, and Reporting	C-3 C-2	6-22-77	6 mo.
006	Applicability of Petroleum Refining Control to Gasification and Other Synfuel Processes	A-5	7-18-77	7 mo
007	Data Possibilities	B-2	8-23-77	9 mo.
008	Preliminary Impact Assessment Input Material Characterization	A-2 A-3	8-23-77	3 mo.
009	Review and Evaluation	C-1	8-25-77	6 mo.

*See Tables 1, 2, and 3 for task descriptions

STATUS OF WORK AUTHORIZED UNDER TECHNICAL DIRECTIVES

The work authorized und[illegible]1 has now been completed. The e[illegible]nsisted of preparation of a work plan [illegible] coordination with other EPA contractors by attending an "all-contractors" meeting. TD 002 and TD 004 will be discussed in more detail below. TD 003 authorizes the preparation of a Technology Overview Report (Task A-1, see Table 1) and the conduct of necessary process engineering studies to support activities authorized under other TD's. Since the Technology Overview Report will be based upon the data base being developed under TD 002, the preparation of this document has been intentionally delayed until significant progress is made in connection with the acquisition and analysis of the data base (TD 002). Because the program has been started only recently, there has been little need to date for process engineering support activities. However, as the work progresses, there will be an increased demand for process engineering support. The work performed under TD 005 has been primarily concerned with program management including reporting to and coordination with EPA.

Many of the control technologies which have been developed for use in petroleum refining would be applicable (in certain cases with some modification) to the synfuel processes. TD 006 authorizes a detailed evaluation of such applicability as part of the control technology evaluation effort in Task A-5. As indicated in Table 4, TD 006 has been issued only very recently. The limited work which has been carried out under this TD consists of collection and review of pertinent key documents on refinery waste/process streams and control technologies.

TD 007, TD 008, and TD 009 have just been issued; the work authorized under these TD's has been restricted to planning activities. Most of the effort in the program to date has been in connection with TD 002, Acquisition and Analysis of the Data Base, and TD 004, Site Locations and Information. Brief descriptions of the accomplishment under these two TD's follow.

TD 002, Acquisition and Analysis of the Data Base.

The acquisition and analysis of the data base are considered the first steps toward detailed environmental assessment of high-Btu gasification. The overall objectives of the effort are to identify the gaps which exist in the available data and the additional data needed for detailed environmental assessment. The activities which have been carried out under TD 002 fall into two categories: data base development and data analysis.

The data base development effort has consisted of identification and acquisition of pertinent documents and establishment of a centralized "high-Btu gasification library" for use by the project personnel. The current library holdings stand at 415 documents consisting primarily of EPA/ERDA reports, symposium proceedings, and journal articles. A system of key word indexing has been developed and used in a computer program which permits easy information retrieval.

Nine gasification systems have been selected as the minimum for detailed analysis in this program. These are Hygas, Bigas, Cogas, Hydrane, Synthane, Texaco, CO_2-Acceptor, Self-agglomerating Ash, and Lurgi. A "modular" approach has been selected for evaluation and presentation of information on these processes. The "modules" which will be addressed are "gasification module," "gas treatment module," "pollution control module," and "integrated facilities." A "data sheet" outline (see Table 5) has been drafted for the presentation of information on the gasification module. Separate "data sheet" outlines are being prepared for the presentation of information on gas purification, pollution control, and integrated facility modules. The use of the data sheet format, which omits lengthy and general process descriptions, is believed to be an excellent means for presentation of key information items, imparting high "visibility" to the engineering "facts and figures," allowing ready comparison of different processes, and underlining areas where significant gaps exist in the available data. The first draft of the gasification data sheet has been completed for six of the nine processes considered (Synthane, Texaco, CO_2-Acceptor, Lurgi, Cogas, and Hydrane). These draft sheets will be updated and revised as more data become available to the program. To assure the accuracy and completeness of the information, it is planned to forward these data sheets to the process developers (ERDA, Texaco Development Company, American Lurgi, and CONOCO) for review and comments.

TD 004, Site Locations, and Information.

As was indicated above, because of the heretofore lack of extensive environmental data on high-Btu gasification processes, the present program places a very strong emphasis on data acquisition through environmental sampling at gasification sites. Obtaining access to a significant number of "important" sites is considered the key to the success of the program. Since six of the nine gasification processes considered are ERDA processes which are being or have been tested at domestic sites, a concentrated effort is currently being directed at exploring sampling opportunities at the ERDA sites. A preliminary meeting has been held with ERDA in Washington to enlist that agency's support for the program. Two possibilities for sampling are being explored: (a) independent sampling at gasification sites and (b) where applicable, "piggybacking" existing and/or planned ERDA environmental sampling and assessment programs (e.g., in connection with Synthane and Bigas Processes). Sampling opportunities at several overseas commercial gasification sites and at one domestic facility operated by a private developer are also currently being explored. Even though the gasification operations at some of these facilities (e.g., the Modderfontein plant in South Africa which uses the Kopper-Totzek Process) result in the production of low-medium Btu gas, these plants have features and processing steps similar to those employed in the production of high-Btu gas.

In connection with TD 004 and in conjunction with the efforts which are or will be carried

TABLE 5

OUTLINE FOR GASIFICATION OPERATIONS DATA SHEET

1.0 GENERAL INFORMATION
  1.1 Operating Principles
  1.2 Development Status
  1.3 Licensor/Developer
  1.4 Commercial Applications
2.0 PROCESS INFORMATION
  2.1 Bench-Scale/Process Development Unit (Figure, Flow Diagram)
    2.1.1 Gasifier
      Equipment
        - Construction
        - Dimensions
        - Bed type and gas flow
        - Heat transfer and cooling
        - Coal feeding
        - Gasification media introduction
        - Ash removal
        - Special features
      Operating Parameters
        - Gas outlet temperature
        - Coal bed temperature
        - Gasifier pressure
        - Coal residence time in gasifier
      Raw Material Requirements
        - Coal feedstock
          Type
          Size
          Rate
        - Coal pretreatment
        - Stream
        - O_2/air
        - Other materials
      Utility Requirements
        - Water
          Boiler
          Quench
          Cooling
        - Electricity
      Process Efficiency
        - Cold gas efficiency
        - Overall thermal efficiency
      Expected Turndown Ratio
      Gas Production Rate/Yield
    2.1.2 Coal Feed/Pretreatment
    2.1.3 Quench and Dust Removal
    2.1.4 Miscellaneous Operations
  2.2 Pilot Plant (Figure, Flow Diagram)
    (Subheadings same as under 2.1 above)
  2.3 Demonstration/Commercial Facilities
    (Subheadings same as under 2.1 above)
3.0 PROCESS ECONOMICS
4.0 PROCESS ADVANTAGES
5.0 PROCESS LIMITATIONS
6.0 INPUT STREAMS
  6.1 Coal
    - Type/origin
    - Size
    - Rate
    - Composition
      Moisture
      Volatile matter
      Ash
      C, etc.
      Minor and trace elements
    - HHV (dry)
    - Swelling number
    - Caking index
  6.2 Steam (temperature and pressure)
  6.3 Oxygen/Air
  6.4 Other Inputs (properties and composition)
7.0 DISCHARGE STREAMS (including unit production rates)
  7.1 Gaseous
    - Stream (x): product gas
    - Stream (y), etc.
  7.2 Liquid
  7.3 Solid
8.0 DATA GAPS AND LIMITATIONS
9.0 RELATED PROGRAMS
REFERENCES

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out under TD 002 (Acquisition and Analysis of the Data Base) and TD 007 (Data Possibilities), information is being collected on the plant flow diagram, waste/process stream accessibility, operating conditions, schedule, etc., for the candidate gasification test sites.

FLUE GAS SAMPLING DURING THE COMBUSTION OF SOLVENT REFINED COAL IN A UTILITY BOILER

Craig S. Koralek and V. Bruce May
Hittman Associates, Inc.
9190 Red Branch Road
Columbia, Maryland 21045

Abstract

Solvent Refined Coal was burned in a commercial utility boiler. Flue gas samples were collected using EPA-5, ASME and Source Assessment Sampling System (SASS) trains and grab sampling methodologies. Results of available analyses are reported.

SUMMARY

On June 10th, 1977 Solvent Refined Coal (SRC) was burned in a commercial utility boiler for the first time, for the purpose of determining whether SRC could replace coal as a primary fuel in a pulverized coal-fired boiler. In addition to boiler efficiency tests, flue gas samples were collected using EPA-5, ASME, and Source Assessment Sampling System (SASS) trains.

In previous phases of this program, coal was burned in the same boiler. Similar tests were performed; results were compared with the Phase III SRC test. The results of the comparison indicate that SRC can be used as a replacement for coal in a conventional pulverized coal-fired boiler. Results of the grab sample analysis indicated no detectable levels of C_1 -C_6 hydrocarbons. SO_2 and NO_x emissions/million Btu were approximately the same as those from burning low sulfur coal. Higher concentrations of NO_x were probably attributable to high combustion temperature or higher organic nitrogen in the fuel, although emissions of NO_x were essentially the same as for coal.

A combustion test at Georgia Power Company's Plant Mitchell, located near Albany, Georgia, was performed to determine whether (SRC) can be burned in a pulverized coal-fired boiler. This three-phase test marked the first time that SRC has been burned in a utility boiler. In addition to boiler and precipitator efficiency tests, a detailed inventory of air emissions, including polynuclear aromatic hydrocarbons, was performed.

In Phase I of this program, low sulfur Kentucky coal was burned in the existing, unmodified 22-1/2 MW pulverized coal boiler. Following replacement of the original burners with dual register burners and accompanying modifications, Phase II of the test was conducted. In this phase, as in Phase I, the boiler was fired with low sulfur Kentucky coal. In Phase III, discussed in detail in this report, following adjustment of the burners and the pulverizers, SRC was burned. This SRC had been produced at the Fort Lewis pilot plant from Western Kentucky coals having a sulfur content of approximately 4 percent and ash content of 10 to 12 percent. Sulfur and ash in the SRC as produced were approximately 0.6 percent and 0.1 to 0.2 percent, respectively. At the time of the combustion test the SRC had been stored onsite in the open for approximately one year. Analytical results showed essentially the same sulfur content but an average ash content of approximately 0.6 percent. However, after removal of certain surface contamination by washing, the ash content of the bulk SRC was in the same range as the ash determination in the material shipped. Further investigation is underway to determine the cause of this difference. In each of the three phases of the program, the boiler was operated at full (~ 21 MW), medium (~ 14 MW), and low (~ 7 MW) load conditions.

Precipitator efficiency tests were run, ash resistivity was determined, and air emission levels were evaluated using EPA-5 and ASME trains. In addition to particulates, a number of gases, including CO_2, CO, NO_x, O_2, and SO_2 were monitored.

During Phases II and III, additional flue gas sampling was conducted using a SASS train to collect samples for a modified EPA Level 1 laboratory analysis. Grab samples also were obtained for on-site analysis for C_1 - C_6 hydrocarbons, SO, N_2, CO, CO_2,and O_2.

A diagram of the SASS train is shown in Figure 1. This sampling device includes

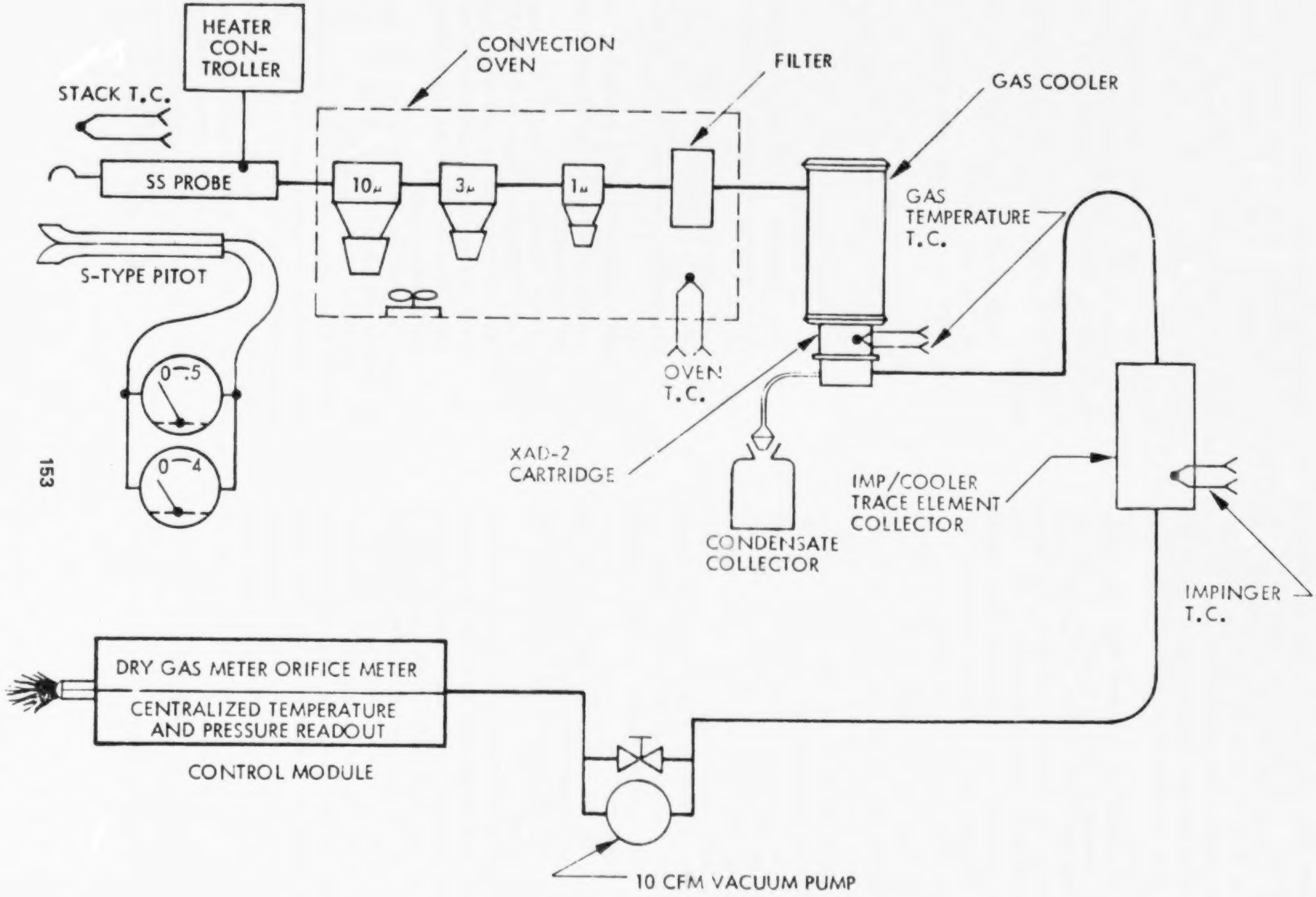
HEATER CON- TROLLER
STACK T.C.
CONVECTION OVEN
FILTER
GAS COOLER
SS PROBE
10μ
3μ
1μ
GAS TEMPERATURE T.C.
S-TYPE PITOT
0–.5
0–4
OVEN T.C.
XAD-2 CARTRIDGE
IMP/COOLER TRACE ELEMENT COLLECTOR
CONDENSATE COLLECTOR
IMPINGER T.C.
DRY GAS METER ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
10 CFM VACUUM PUMP

Figure 1. Source assessment sampling schematic.

cyclones and a filter to collect particulates, a sorbent trap to collect C_7 - C_{16} hydrocarbons, impingers, and associated temperature controls, pumps, and meters. The sample is obtained from the flue gas duct by means of a probe inserted through the duct work and positioned to intersect the gas flow at a point having flow characteristics representative of the bulk flow.

Particulates are removed from the sample first, passing it through a series of cyclones. For the SRC tests, these cyclones were maintained at a temperature of 400 F. Particulates are collected in three size ranges, $> 10\mu$, 3 to 10μ , and 1 to 3μ , respectively. The cyclones are followed by a standard fiberglass filter, which collects a fourth size range, $< 1\mu$.

Gas leaving the filter is cooled to approximately 68°F and passed through a cartridge containing XAD-2 resin. This resin absorbs a broad range of organic compounds. Condensate produced when the gas is cooled is collected in a condensate trap.

A series of three impingers follows the resin cartridge. The first contains hydrogen peroxide solution, which removes reducing components to prevent deterioration of the following impinger solutions. The second and third impingers, containing ammonium thiosulfate and silver nitrate, collect volatile inorganic trace elements.

Next, the gas passes through a dehydrating agent, to protect the pump which follows. Finally, the gas flow rate is metered, and the gas is vented.

Using the SASS train, each test run provided a total of nine samples, all of which included solids fractions, condensate, resin, impinger liquids, and rinses. After weighing, several of the initial samples were combined for further analysis. Results will indicate the presence or absence of several classes of organic compounds as well as inorganic components and trace elements. In addition to the abbreviated Level 1 anaysis, the samples will be analyzed to determine whether or not selected polynuclear aromatic compounds, having carcinogenic properties, were present.

Grab samples of the flue gas were collected using a Tedlar bag and a stainless steel probe. The samples were extracted from the stack by means of varistaltic pump, which can obtain leak-free samples over a short period of time. On-site analysis was performed (usually within thirty minutes of sampling) by injecting gases captured in the sample bag into a gas chromatograph. Parameters identified included C_1 - C_6 hydrocarbons, CO, SO_2, O_2, N_2, and CO_2.

Daily composites of the coal used during Phase II and the SRC used during Phase III were also prepared. Bottom ash samples were collected as well.

Participants in the SRC combustion tests included:

- Southern Company Services — co-sponsor and owner
- ERDA — co-sponsor and supplier of SRC
- Southern Research Institute (SRI)-SASS Train Sampling and Resistivity
- TRW — Grab sampling and on-site analysis for CO, CO_2, SO_2, N_2, O_2, and C_1 - C_6 hydrocarbons.
- York Research — EPA-5 and ASME trains, gaseous emissions, precipitator efficiency
- Babcock & Wilcox — Boiler efficiency
- Rust Engineering (Subsidiary of Wheelabrator-Frye) with SRI — Resistivity;
- Wheelabrator-Frye — modeling of precipitator for control of SRC combustion particulates
- Hittman Associates, Inc. — Development of sampling plan for the SASS train and grab samples, coordination of these efforts, and responsibility for subsequent SASS train sample analysis and interpretation.

Figure 2 depicts the location of the precipitator and sampling ports. Boiler #1 was the test boiler. Load conditions (i.e., full, medium, and low) were varied daily. During the first nine days of testing, samples were collected at the inlet and outlet of precipitator #1. Test ports A_1, A_2, B_1, and B_2 were used for this emission testing. ASME and EPA-5 trains were used simultaneously to collect samples both at inlet ports A_1 or A_2, and outlet ports B_1 or B_2. SASS train samples and grab samples for on-site analysis were collected either at inlet

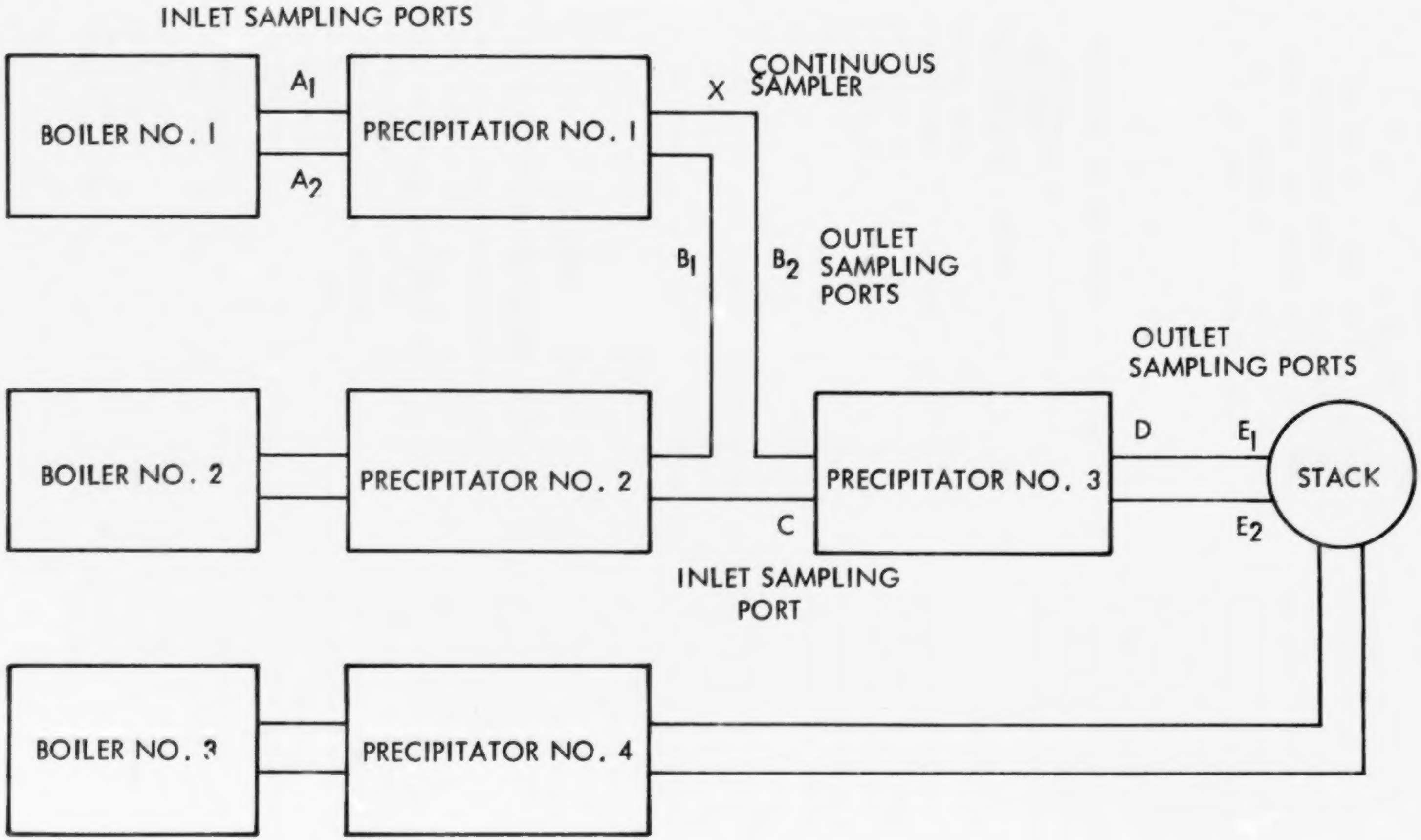
INLET SAMPLING PORTS
BOILER NO. 1
A_1
A_2
PRECIPITATIOR NO. 1
X
CONTINUOUS SAMPLER
B_1
B_2
OUTLET SAMPLING PORTS
OUTLET SAMPLING PORTS
BOILER NO. 2
PRECIPITATOR NO. 2
PRECIPITATOR NO. 3
D
E_1
STACK
E_2
C
INLET SAMPLING PORT
BOILER NO. 3
PRECIPITATOR NO. 4

Figure 2. The location of the boilers, precipitators and sampling ports at Plant Mitchell.

port A_1 or outlet port B_1. Point X indicates the location of the continuous sampler for monitoring gases such as SO_2 and NO_x.

Since precipitator #1 is a 1946 vintage Research Cottrell unit with perforated plates, Rust Engineering and Wheelabrator-Frye requested that two additional days of tests be performed on precipitator #3, a newer, more up-to-date,unit. Data gathered could be used in the future for modeling purposes. To facilitate these tests, boiler #2 and precipitators #1 and #2 were shut down. Samples were collected at ports C, D, E_1 and E_2. ASME and EPA-5 samples were simultaneously collected at ports C, E_1, and E_2. SASS train and grab samples for on-site analysis were collected at outlet port D.

PHASES II & III TESTING

In both Phase II, coal combustion, and Phase III, SRC combustion, the boiler was operated at full, medium and low load conditions. In addition, at the conclusion of Phase III, the boiler was operated "wide open", approximately 23.5 MW, for several days.

Because only one SASS train was available, it was impossible simultaneously to collect samples at both the inlet and outlet ports to the precipitator. During each phase the SASS train location was varied to permit sampling at both ports. During each SASS run, a grab sample for on-site analysis was collected at the same location. EPA-5 and ASME trains operated concurrently at both the inlet and outlet of the precipitator being tested and while the SASS train was in operation.

The schedules for Phases II and III were developed by Mr. Richard McRanie of Southern Company Services after consultation with participants. The load condition and test precipitator were designated for each day of testing. Tables 1 and 2 indicate these schedules as well as the sampling location for the SASS train.

During Phase II, which began May 24, 1977, low sulfur Kentucky coal was burned in the boiler. No significant operational problems were noted during this phase. The burners operated as expected and flue gas samples were collected. Phase II concluded on June 6, 1977, after eleven days of testing.

Combustion of SRC, Phase III, began on June 10th, 1977. Sampling began on June 13, 1977 and continued through June 24, 1977. A few additional days of testing were scheduled starting June 25th; however SASS and grab samples were not collected because of the experiments being conducted. The schedule called for variation in load levels, air to SRC feed ratios, and precipitator rapping. Because

TABLE 1

PHASE II - COAL COMBUSTION TEST SCHEDULE

Date	Load Condition	SASS Train Sampling Location
May 24	Full	Outlet ESP #1
May 25	Medium	Outlet ESP #1
May 26	Low	Outlet ESP #1
May 27	Full	Outlet ESP #1
May 28	Full	Inlet ESP #1
May 29	Medium	Inlet ESP #1
May 30	Medium	Outlet ESP #1
May 31	Low	Outlet ESP #1
June 1	Low	Inlet ESP #1
June 5	Full	Outlet ESP #3
June 6	Full	Outlet ESP #3

TABLE 2

PHASE III - SRC COMBUSTION TEST SCHEDULE

Date	Load Condition	SASS Train Sampling Location
June 13	Full	Outlet ESP #1
June 14	Medium	Outlet ESP #1
June 15	Low	Outlet ESP #1
June 16	Full	Outlet ESP #1
June 17	Full	Inlet ESP #1
June 18	Low	Inlet ESP #1
June 19	Low	Outlet ESP #1
June 20	Medium	Inlet ESP #1
June 21	Medium	Outlet ESP #1
June 22	Full	Outlet ESP #3
June 23	Full	Outlet ESP #3
June 24	"wide open"	Outlet ESP #1

of the short duration of these conditions, it was impossible to complete a SASS train run which typically is of five-hour duration.

ANALYTICAL RESULTS

Results of the SASS train analyses are not available at this time. Figure 3 shows the planned analytical procedures. Samples from both Phase II (coal) and Phase III (SRC) runs will be analyzed. One coal and one SRC sample also will be tested for trace elements.

Results which are available at this time include the on-site analyses presented in Tables 3 and 4. Analyses of the coal and SRC, and calculated emissions are presented in Tables 5, 6, and 7.

The C_1 to C_6 hydrocarbons were determined by means of a flame ionization detector in a Perkin-Elmer gas chromatograph. During the first three days of Phase II, the test limits were 5 ppm due to improper grounding of the instrument. During the remainder of the tests, the detectable limit was 0.5 ppm. The O_2, N_2, CO and CO_2 and SO_2 levels were measured with a thermal conductivity detector in an A.I.D. portable gas chromatograph. The accuracy of this instrument is ± two percent of the reading taken.

NO_x and SO_2 were continuously monitored. Thermo electron analyzers were used to measure nitrogen oxides and sulfur oxides. The accuracy of these instruments is ± 10 ppm.

Results of the on-site analysis of grab samples are included in the following section of this report. The following conclusions can be drawn about SRC combustion:

- When compared on a pounds of SO_2 per million Btu basis, SRC flue gas shows only approximately 67 percent as much SO_2 discharge as does coal flue gas, during the course of this test.
- When the coal sulfur content was approximately the same as the SRC sulfur content, SO_2 emissions per million Btu were equivalent.
- Pounds of NO_x per million Btu are lower in the SRC flue gas than in the coal flue gas, by approximately 15 percent, during the course of this test.
- O_2 levels during SRC runs ran slightly below levels measured in coal combustion. This is directly related to control room operations. Control room data will be available later.
- SO_2 and NO_x concentrations were highest at full load and lowest at low load conditions.
- C_1 - C_6 hydrocarbons were not detected during either Phase II or Phase III. The detection limit for these components was 0.5 ppm.

OBSERVATIONS AND CONCLUSIONS

No major problems were encountered with the combustion of SRC. Generally, the boiler operated smoothly. On Wednesday, June 15th, however, fire was lost in the boiler for about one hour and the SASS train run was lost. The cause of the problem was believed to be failure of the fuel to reach the burner. This could not directly be attributed to the SRC. Another run was lost when pieces of polyethylene sheet, upon which the SRC was stored, were accidentally scooped up by the front end loader removing the SRC from the storage pile, and fed into the pulverizers. The pulverizers jammed and the run was cancelled.

Results of the test are limited at this time. Future analytical results will be incorporated in a final report. The following preliminary observations can be made. These observations were made either in the field or during preparation of samples for shipment to the laboratory.

- Particulates collected by the SASS train during combustion of SRC were approximately seventy percent carbon. This compares with a typical coal fly ash carbon content of less than ten percent. The high level of carbon is probably due to the boiler type. This 22-1/2 MW boiler was originally designed to burn oil, later modified to burn coal, and further modified prior to Phase II testing. In addition, since the ash content of SRC is much lower than that of coal, identical combustion efficiencies for coal and SRC would result in a proportionately higher carbon content in the fly ash, even though the

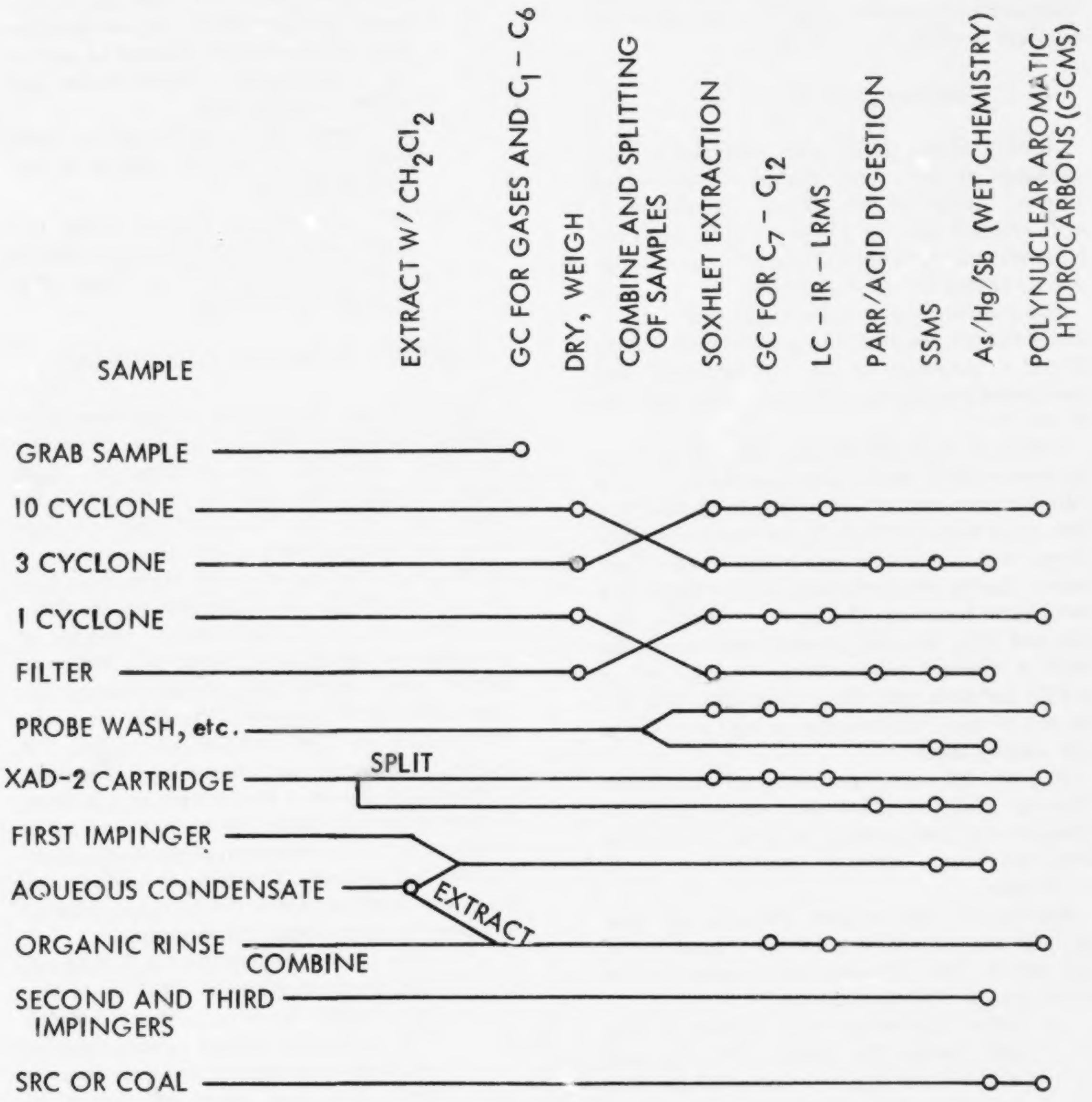
SAMPLE
EXTRACT W/ CH2Cl2
GC FOR GASES AND C1 – C6
DRY, WEIGH
COMBINE AND SPLITTING OF SAMPLES
SOXHLET EXTRACTION
GC FOR C7 – C12
LC – IR – LRMS
PARR/ACID DIGESTION
SSMS
As/Hg/Sb (WET CHEMISTRY)
POLYNUCLEAR AROMATIC HYDROCARBONS (GCMS)
GRAB SAMPLE
10 CYCLONE
3 CYCLONE
1 CYCLONE
FILTER
PROBE WASH, etc.
XAD-2 CARTRIDGE
SPLIT
FIRST IMPINGER
AQUEOUS CONDENSATE
EXTRACT
ORGANIC RINSE
COMBINE
SECOND AND THIRD IMPINGERS
SRC OR COAL

Figure 3. Analytical schematic.

TABLE 3

ON-SITE ANALYSIS OF GRAB SAMPLES PHASE II · COAL COMBUSTION
MAY 24 TO JUNE 6, 1977

	On-Site Gas Chromatograph Analysis											Continuous Sampler				
Date	C_1 (4)	C_2 (4)	C_3 (4)	C_4 (4)	C_5 (4)	C_6 (4)	CO (3)	O_2 (1)	CO_2 (1)	N_2 (1)	SO_x (1)	SO_x (2)	NO_x (2)	Time	Load Condi-tion	Sample Loca-tion
5/26	ND	ND	ND	ND	ND	ND	ND	13.31%	7.40%	79.29%	254	260	110	1500	Low	0-1
5/31	ND	ND	ND	ND	ND	ND	ND	14.24%	7.50%	78.26%	329	360	110	1140	Low	0-1
6/02	ND	ND	ND	ND	ND	ND	ND	14.91%	6.56%	78.53%	174	200	100	0300	Low	I-1
5/25	ND	ND	ND	ND	ND	ND	ND	15.73%	5.51%	78.76%	413	500	170	1400	Med	0-1
5/29	ND	ND	ND	ND	ND	ND	ND	13.70%	7.59%	78.71%	209	220	160	1400	Med	I-1
5/30	ND	ND	ND	ND	ND	ND	ND	12.60%	7.35%	80.05%	413	400	150	1240	Med	0-1
5/24	--	--	--	--	--	--	--	------	-----	------	---	745	225	1200	Full	0-1
5/27	ND	ND	ND	ND	ND	ND	ND	13.78%	6.65%	79.66%	311	330	215	1530	Full	0-1
5/28	ND	ND	ND	ND	ND	ND	ND	11.25%	9.86%	78.89%	381	330	220	1420	Full	I-1
6/05	ND	ND	ND	ND	ND	ND	ND	12.14%	9.31%	78.55%	214	200	170	1330	Full	0-3
6/06	ND	ND	ND	ND	ND	ND	ND	11.16%	9.69%	79.15%	210	180	110	1030	Full	0-3

ND - None Detected

I-1 - Inlet to precipitator - 1

0-1 - Outlet to precipitator - 1

0-3 - Outlet to precipitator - 3

SO_x and NO_x values are in ppm

(1) - ± 2% of total concentration

(2) - ± 10 ppm

(3) - 40 ppm detectable limit

(4) - 5 ppm detectable limit 5/25, 5/26, and 5/27, 0.5 ppm detectable limit 5/28 through 6/06

TABLE 4

ON-SITE ANALYSIS OF GRAB SAMPLES PHASE III - SRC COMBUSTION
JUNE 13 TO JUNE 24, 1977

	On-Site Gas Chromatograph Analysis											Continuous Sampler				
Date	C_1(4)	C_2(4)	C_3(4)	C_4(4)	C_5(4)	C_6(4)	CO(3)	O_2(1)	CO_2(1)	N_2(1)	SO_x(1)	SO_x(2)	NO_x(2)	Time	Load Con-dition	Sample Location
6/15	ND	ND	ND	ND	ND	ND	ND	14.79%	5.88%	79.33%	198	225	125	1030	Low	0-1
6/18	ND	ND	ND	ND	ND	ND	ND	13.25%	6.73%	80.02%	216	220	120	1200	Low	I-1
6/19	ND	ND	ND	ND	ND	ND	ND	14.00%	6.26%	79.74%	218	235	125	1230	Low	0-1
6/14	ND	ND	ND	ND	ND	ND	ND	13.65%	7.53%	78.82%	248	260	160	1200	Med	0-1
6/20	--	--	--	--	--	--	--	------	-----	------	---	---	----	----	Med	0-1
6/21	--	--	--	--	--	--	--	------	-----	------	---	---	----	----	Med	I-1
6/13	ND	ND	ND	ND	ND	ND	ND	11.39%	9.86%	78.75%	371	325	190	1300	Full	0-1
6/16	ND	ND	ND	ND	ND	ND	ND	10.62%	9.12%	80.26%	410	335	190	1145	Full	0-1
6/17	ND	ND	ND	ND	ND	ND	ND	11.11%	9.15%	79.74%	404	345	190	1100	Full	I-1
6/22	ND	ND	ND	ND	ND	ND	ND	11.20%	9.25%	79.55%	400	345	200	1030	Full	0-3
6/23	ND	ND	ND	ND	ND	ND	ND	10.75%	8.90%	80.35%	393	325	220	1000	Full	0-3
6/24	ND	ND	ND	ND	ND	ND	ND	10.76%	9.29%	79.95%	449	380	260	1100	23.5	0-1

ND - None Detected

I-1 - Inlet to precipitator-1

0-1 - Outlet to precipitator-1

(1) - ± 2% of total concentration

(2) - ± 10 ppm

(3) - 40 ppm detectable limit

(4) - 0.5 ppm detectable limit

0-3 - Outlet to precipitator-3

SO_x and NO_x values are in ppm

TABLE 5

SRC COMBUSTION TEST - PHASE II, COAL

	Proximate Analysis				SO_2, ppm		NO_x, ppm
Date	% Sulfur	% Nitrogen	Heating Value, Btu/lb (1)	Load	Grab Sample	Continuous Analyzer	
5/26	0.64	1.38	14935	Low	254	260	110
5/31	1.05	1.81	14723	Low	329	360	110
6/2	NA	NA	NA	Low	174	200	100
5/25	1.09	1.29	14648	Med	413	500	170
5/29	0.62	1.82	14923	Med	209	220	160
5/30	1.15	1.82	14725	Med	403	400	150
5/24	1.34	1.19	14720	Full	NA	745	225
5/27	0.73	1.51	14802	Full	311	330	215
5/28	0.72	1.45	14797	Full	381	330	220
6/5	0.66	1.60	NA	Full	214	200	170
6/6	0.64	1.81	14931	Full	210	180	110

NA - Not Available
(1) Moisture and Ash Free Basis.

TABLE 6

SRC COMBUSTION TEST - PHASE III, SRC

	Proximate Analysis				SO_2, ppm		NO_x, ppm
Date	% Sulfur	% Nitrogen	Heating (1) Value, Btu/lb	Load	Grab Sample	Continuous Analyzer	
6/15	0.70	1.54	15742	Low	198	225	125
6/18	0.74	1.80	NA	Low	216	220	120
6/19	0.66	1.82	15668	Low	218	235	125
6/14	0.72	1.62	15729	Med	248	260	160
6/13	0.73	2.02	15591	Full	371	325	190
6/16	0.73	1.77	15602	Full	410	335	190
6/17	0.72	1.47	15775	Full	404	345	190
6/22	0.70	1.37	15647	Full	400	345	200
6/23	0.64	1.37	15534	Full	395	325	220
6/24	0.66	1.71	15505	Wide Open	449	380	260

NA - Not Available

(1) Moisture and Ash Free Basis

TABLE 7

RUN NUMBER, PRECIPITATOR NUMBER 1

	Run Number, Precipitator Number 1								
Conditions	1	2	3	4	5	6	7	8	9
Coal									
Date	5/24	5/25	5/26	5/27	5/28	5/29	5/30	5/31	6/1
Load, MW	21	14	6	21	21	14	14	7.5	7.5
Fuel Feed, lb/hr	22,300	15,300	7,400	21,000	20,000	15,000	15,000	9,400	9,700
SO_2 lb/10^6 Btu	2.33	1.86	1.50	1.03	1.06	1.84	1.84	2.38	1.39
NO_x lb/10^6 Btu	0.50	0.45	0.46	0.48	0.51	0.50	0.50	0.52	0.50
SRC									
Date	6/13	6/14	6/15	6/16	6/17	6/18	6/19	6/20	6/21
Load, MW	21	14	7.5	21	21	7.5	7.5	14	14
Fuel Feed, lb/hr	17,500	12,000	7,200	17,800	17,600	7,400	7,400	12,000	12,200
SO_2 lb/10^6 Btu	0.99	1.02	1.21	0.97	1.01	1.05	1.13	1.11	1.04
NO_x lb/10^6 Btu	0.41	0.45	0.48	0.39	0.40	0.41	0.41	0.49	0.45

total carbon in the ash might be the same.

- The total quantity of fly ash produced from SRC combustion is approximately ten percent of that resulting from the coal normally used at this facility.
- The aerodynamic particle size of SRC ash was much smaller than that of coal fly ash. It is estimated that two to five percent of coal fly ash collected in Phase II was less than one micron. Comparably, approximately twenty percent of the SRC fly ash was collected on the filter following the one micron cyclone.

  It should be noted, however, that due to the low density of the SRC ash, particles which should have been collected by the one micron cyclone instead may have passed through the cyclone and collected on the filter. The cyclones in the SASS train were designed to collect particles having the density of coal fly ash, i.e., 1 g/ml. SRC fly ash is approximately one-fifth as dense as coal fly ash. It was observed that, with SRC, the filter had to be changed frequently during each daily test, indicating that after a certain volume of particulate was collected in the cyclone, particles began passing through the 1 micron cyclone or the particulates collected were agitated and suspended in air, finally collecting on the filter.
- The efficiency of precipitator #1 with SRC ash was estimated by the ERDA Sampling Team to be at best twenty percent. The hoppers to the precipitator were checked and no ash had been collected. The low efficiency of the precipitator is probably due to the low resistivity and density of the high carbon fly ash.

  During the latter part of Phase III, when precipitator #1, boiler #2, and precipitator #2 were shut down, the efficiency of collection by precipitator #3 was significantly higher than observed with precipitator #1. Partical loading at the outlet totaled approximately 1 gram. This compares with about 25 grams for a similar full load test at the outlet to precipitator #1. The filter following the cyclones did not have to be changed during tests at the outlet to precipitator #3. Up to five filter changes had been needed during tests at both the inlet and the outlet to precipitator #1.

  There was a visible plume on all SRC combustion tests using precipitator #1. The opacity was estimated at Ringelman 2. However, when only precipitator #3 was functioning, there were no visible emissions. During coal combustion, there was evidence of a plume on occasion. Boiler #2, which was shut down when tests were run around precipitator #3, may be the cause of the visible plume. It was suggested that without boiler #2 flue gas feeding into precipitator #3, the unit, which is oversized, was effective.
- Although approximately equal volumes of ash were collected from both coal and SRC combustion, about 50 percent less fly ash, by weight, was collected during the SRC tests.
- Some dusting was noted during handling of SRC. A front end loader was used to load a dump truck which in turn emptied into the feed hopper. It was difficult to assess accurately the potential magnitude of this problem, since this method of handling is not standard operating procedure at the plant.

Generally, the SASS train performed adequately. On most occasions, representative flue gas samples were collected. There were, however, several problem areas.

- The SASS train equipment proved to be very cumbersome. This problem was aggravated by space limitations.
- An electrical generator had to be rented in order that an adequate supply of electricity (45 amps) was available. Two runs on Phase III were lost when the generator broke down.
- The entire SASS train operation, including preservation of samples and preparation of the equipment for the

next run, required 10 to 12 hours. Three men were required for this labor intensive effort.

- As mentioned earlier, the cyclones were designed to collect particulates with a density comparable to coal fly ash. SRC fly ash, which has one-fifth the density of coal fly ash, may have passed through the cyclones. This may explain why filters had to be changed so frequently. Each time a filter had to be changed, the run had to be stopped, the filter cooled and removed, and the oven reheated. Each filter change required a delay of up to thirty minutes. This may have caused an erroneous particle size distribution since particles may have passed through to the next smaller cyclone or to the filter.
- Because the particulates were extremely light and fine, small amounts of particulate were lost during the subsequent transfer to the plastic sample containers.
- Because of the time constraints, it was impractical to soak the SASS train in 1:1 nitric acid following each run. If this procedure, prescribed in the operator's manual, had been followed, it would have been impossible to both preserve the samples and prepare for the next day's operation.

ENVIRONMENTAL AND ENGINEERING EVALUATION OF THE KOSOVO COAL GASIFICATION PLANT, YUGOSLAVIA

by

Becir Salja and Mira Mitrovic
Kombinat Kosovo, Obilic-Pristina
and
Mining Institute, Beograd-Zemun
Yugoslavia

Abstract

Lignite gasification is presently a worldwide process. Around the world, researchers are involved in obtaining an improved form of power from all kinds of coal as well as a more efficient and economical recovery of the coal substance itself. In the United States there is also a great interest in producing a low- and medium-Btu gas from coal. In this context, an assessment of environmental problems arising from such technological processes coupled with the development of techniques for their reduction or elimination are of great importance. The Environmental Protection Agency has initiated and is carrying out a broad research program on the above problems together with various corporations in the United States.

Within the range of operations of the program on Scientific-Technological Cooperation between the United States and Yugoslav governments, EPA has also initiated such investigations in Yugoslavia. Yugoslavia harbors substantial lignite reserves that are primarily used for electric power generation. In addition, great efforts are devoted to the development of an extremely adequate and economical technology for lignite processing. In Obilic, near Pristina, a commercial plant has been erected and put on stream for gas production from Kosovo lignite according to the Lurgi Process.

This paper outlines the research program carried out in the plant for the production of gas under pressure with a net heating value of 3600 kcal/m^3_N *on the basis of lignite dried by the Fleissner Process. The plant consists of six Lurgi gasifiers, each 3.6 m in diameter. The annual output is 480 mil* m^3_N *of clean gas. The research program includes: process description (ratio of masses and composition of major charges and output streams); description of measurement points; sampling; analysis and identification of major and minor pollutants; evaluation of resulting data and methods used in the investigations; determination of the amounts of individual pollutants; preparation of gasification process thermal balance and preparation of sulphur material balance. Analysis and identification of pollutants is performed on emissions discharged into the atmosphere, waste waters, and solid residues of the gasification process (dust, slurry, and slag). Three ambient samples are also analysed.*

In addition, the paper indicates the problems encountered during the conversion of low-heating value Kosovo lignite into gaseous fuel by the Lurgi Process.

INTRODUCTION

An accelerated effort is currently underway in the United States to develop advanced coal gasification technology to provide an alternate source of energy. Inherent in the application of this developing technological area is the need to assess the environmental problems of these processes and to develop techniques to reduce or eliminate these problems.

The first phase of this assessment is the identification and quantification of pollutants in existing similar processes. Presently, there are no commercial coal gasification plants operating within the United States; therefore, any investigation must be conducted outside the borders of the U.S.A.

Preliminary data acquisition from pilot operations has indicated that a multiplicity of pollutants are emitted by the gasification reactor. Materials found in effluent and process streams include major pollutants, such as sulfur, nitrogen, NH_3^+, particulate tars and oils, and minor pollutants, such as trace elements and hydrocarbons. A comprehensive analysis providing the composition and levels of major and minor pollutants found in the process and various effluent streams will provide a basis for the determination of the potential environmental degradation accompanying the gasification process and for the evaluation of currently utilized clean-up and purification systems.

By initiating test programs in foreign countries EPA is currently utilizing the various coal gasification processes and steps are being taken to develop the methodology and necessary pollutant control equipment before the construction of commercial full scale gasification plants in the U.S.A.

Data acquired in these foreign studies will supplement information currently being acquired in pilot plant test programs in U.S.A.

In Yugoslavia similar efforts are underway.

Yugoslavia has in situ considerable deposits-resources of lignite. Although lignite is used primarily as a fuel to generate heat and power, at the present time, the research is underway to develop the most adequate and economical process technology for conversion of lignite (fuel of low caloric value) to synthetic gas and liquid fuels.

In Socialist Autonomous Province Kosovo a commercial gasification plant has been erected and is in operation using Lurgi procedure for gas production from Kosovo-lignite.

All above mentioned facts prove the significance of the problem. On the basis of the agreement about scientific and technological cooperation between American and Yugoslav Governments, the following organizations:

- Environmental Protection Agency from the United States of America,
- Rudarski Institut - Beograd, and
- REMHK Kosovo - Obilic, Socialist Autonomous Province Kosovo,

made out a programme and agreed upon the project statement for the research project entitled: "Environmental and Engineering Evaluation of the Kosovo Coal Gasification Plant."

The research work under this project will be carried out by:

- Research and Development Department REMHK Kosovo - Obilic, and
- Rudarski Institut - Mineral Dressing Department, Beograd.

The project is to be completed within 3 years from the date of signing. The project officer is Mr. Kelly Janes, chemical engineer from EPA, USA.

The principal researcher is Mr. Becir Salja, dipl. chem. from REMHK Kosovo-Obilic.

Mrs. Mira Mitrovic, chemical engineer is responsible for the part of work carried out at Rudarski Institut.

The objective of the research is therefore to identify and quantify pollutants in existing gasification processes in order that improved techniques can be developed to reduce or eliminate environmental injury resulting from implementation of one such technology. Specific objectives will be the identification of composition and levels of major and minor pollutants of all process streams and the identification and levels of all pollutants in the various effluent streams or materials (air, water, solids). Determination of the fate of pollutants, allowing for the evaluation of potential environmental degradation, and a study of the effectiveness of present day clean-up and purification systems will also be made. Priority will be given to quantification of major pollutants, i.e., sulfur, nitrogen, NH_3^+, particulate tars, and oils in the initial phase (I). Subsequent investigations will study the minor or trace pollutants in phase II.

The investigations should result in the selection of sample analysis methods to be applied.

The following text is comprised of:

- date of Kosovo Lignite Gasification Plant by Lurgi Procedure,
- investigation Programme (Phase I and Phase II) and Methodology for determination of gaseous, liquid, and solid pollutants contained in air, water, and solid wastes, and
- observed problems relevant for above theme.

GAS PRODUCTION FROM LIGNITE KOSOVO

In Obilic, near Pristina, Socialist Autonomous Province Kosovo, a plant was erected and started up for the production of gas under pressure (clean gas net heating value 3600 Kcal/m_N^3) from dried Kosovo lignite (Lurgi generators, Dia 3.6 m). The plant capacity is 480 million m_N^3 of clean gas per annum, representing only the first phase of Kosovo gasification plant. According to the long-term development program for this coal basin, total gas production should reach approximately 1500 million m_N^3 per year.

The specific purpose of the gas as a power fuel for the requirements of Steel Works Skopje and surrounding industry, i.e., as a raw material for nitrogen fertilizer production in Obilic, was significant in deciding on the erection of the gasification plant in Kosovo Basin.

The Kosovo Basin Gasification Plant includes the following sections:

- gas generators: 6 generators with a capacity of 18,000 m_N^3 of crude gas each, with coal feeding and slag disposal arrangements,
- condensation,
- "rectisol" installation for gas cleaning with gas delivery station,
- air decomposition plant,
- tar and medium oil separation,
- "phenosolvent" installation for phenol separation, and
- installation for biological wastewaters cleaning.

Gasification plant feed consists of dried lignite according to the "Fleissner" method with a size range - 60 + 6 mm.

Of the mentioned amount (480 · 10^6 m_N^3/year), 77 percent is further processed in order to remove the hydrogen required for ammonia synthesis. The residue is a methane enriched fraction mixed with the remaining clean gas. This mixture (256 · 10^6 m_N^3/year) represents the pipeline gas with a net heating value of 4000 Kcal/m_N^3/year, supplied into the gasline system.*

Material and Power Balances of Kosovo Lignite Gasification*

Feed		
Dried coal (–60+6 mm)	86t/h	688,000 t/year
95 percent oxygen	11,560 Nm^3/h	92.5 x 10^6 Nm^3/year
Steam, 30 atm	74 t/h	592,000 t/year
Electric power	9,730 kWh	77,840 MWh/year
Phenosolvent (diizopropilether)	–	–
Methanol	56 kg/h	448 t/year
Hydrocloric acid	4 kg/h	32 t/year
Sodium-hydroxide	2.5 kg/h	20 t/year
Aluminum sulphate	2.5 kg/h	20 t/year
Output		
Cleaned gas	60,000 Nm^3/h	480 x 10^6 Nm^3/year
Tar	2.2 t/h	17,600 t/year
Oil	1.0 t/h	8,000 t/year
Crude gasoline	7.5 t/h	60,000 t/year
Gas water	90 Nm^3/h	720,000 m^3/year
Carbon dioxide	25,000 Nm^3/h	200 x 10^6 Nm^3/year

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*Data taken from the project.

PROGRAM OF INVESTIGATION

The research program includes the following tasks:

Phase I:

1. Process description (ratio of masses and composition of major feeds and outlet streams),
2. Sampling and analysis of major pollutants occurring in large quantities, determination of mass ratios and compositions of major feeds and outlet streams.

Note:

a. Sampling is carried out simultaneously on all measurement points while the plant is operating under constant condition over an 8-hour period. The samples are divided and processed in two laboratories,

b. Sampling campaign completed according to the following schedule:
   - test run,
   - first campaign,
   - second campaign,
   - third campaign, and
   - repeated testing if required.

3. Evaluation of test data acquired by processing the pollutants occurring in large quantities and the methods used during the tests.
4. Identification of trace pollutants (Phase II).
5. Evaluation of data acquired by process-

ing the pollutants occurring in small quantities and evaluation of the effectiveness of methods used for analyses (Phase II).

6. Heat Balance for Gasification Process on the basis of determined statistical data on the amounts and heating value of the coal consumed for:
   - a . gasification (dried lignite)--generators
   - b . heat generation (raw mine coal)--steam production for the generators, etc.

     as well as for:
   - c . the heat consumed in the gasification process, and on the basis of determined calories in:
   - d . the produced gas, and
   - e . liquid products.

Lignite heat recovery will be calculated for the Lurgi process of gasification.

7. Sulphur material balance in the process of Kosovo lignite gasification:
   - a . *Feed:*
     - Coal
   - b . *Outputs:*
     - synthesis gas and medium BTU gas,
     - tar (storage),
     - medium oil (storage),
     - gasoline (storage),
     - phenol (storage),
     - discharges into the atmosphere,
     - waste waters,
     - gasification slag (disposal area), and
     - heavy tar and coal dust (disposal area).
8. Final report with the evaluation of the technological process and environmental pollution, from Kosovo lignite gasification by "Lurgi" procedure and possible improvement proposals.

   Pollutants determination includes:
   - a . Control of Air Emissions

     Analyses:

     H_2S
     Phenols
     Ammonia
     Particulate
     CO_2
     SO_x
     COS
     NO_x
     Hydrocarbons
   - b . Control of Generator Wastewaters

     Analyses:

     COD
     BOD_5 (dilution method)
     Permanganate Value
     Phenols, volatile and nonvolatile
     Ammonia, free and fixed
     Cyanide
     Hydrogen sulfide
     Tar oil (ether extracts)
     Suspended solids
     Dry solids (105° C and 850° C)
     pH value
     Chloride
     Sulfates
     Rhodanate, Thiosulfates
     Fluorides, Nitrites, Nitrates, Sulfites
   - c . Control of Solid Wastes from the Coal Gasification Process (Sludges and Dusts from Gas Purification Slag and Ash)

     Analyses:

     Moisture
     Dry solids (105° C and 850° C)
     Ash composition
     Phenol, total and volatile, in water filtrate
     Elementary analysis of dry material (105° C)
     COD (water filtrate)
     BOD (water filtrate)

Notice: All pollutants will be determined as to ASTIM procedure.

In studying the foregoing research program, due consideration should be paid to the following:

- Location of sampling points, fitting the required sampling connections, and installation of platforms and accesses for sampling.
- Repair and calibration of all equipment, purchased and borrowed, in order to secure adequate operation.
- Preparation of test schedule, together with a list of sampling methods,

methods for sample preparation and selection of analysis methods (ASTM).

- Compilation of plant operative data over the test period.
- Provision of the equipment required for the analysis of samples, representative samples will be taken and appropriately preserved. Repeated double analyses will be performed.
- Regular preparation of reports on the results of works during a reasonable period upon analyses completion.

Specific key streams will be sampled in the Kosovo Coal Gasification Plant, and appropriate analyses will be carried out in accordance with the information supplied below:

Figure 1--Sampling points (plant streams and ambient)

The samples presented in Figure 1, found enclosed, are considered the most useful ones for initial research in this plant. A total of 19 sampling points has been located for gaseous, liquid, and solid samples. Table 1 (enclosed) includes the sample to be taken, required stream measurements, analyses of trace elements and trace organic materials, GCMS, HPLC, and AA analyses and size comprise determinations.

General locations of area sampling points are also indicated on Figure 1. Three area samples are to be taken at locations to be selected.

In area samples (three), the following components will be determined by use of appropriate methods:

ANALYSIS	METHOD
CO	NDIR
NO_x	Chemiluminescent
SO_2	
H_2S	FPD/GC
COS	
CS_2	
Mercaptans	
HC	FID/GC
Particulates	Hi Vol
Organics	XAD-2/GCMS

DESCRIPTION OF THE TECHNOLOGICAL PROCESS AND SAMPLING POINTS IN COAL GASIFICATION PLANT KOSOVO

Figure 1 presents the flow sheet of Coal Gasification Plant Kosovo and the sampling points in the process streams and area.

Sampling will be carried out in the following plant sections:

- Generators (Figure 2),
- Condensation and tar separation (Figures 3 and 4),
- Rectisol (Figure 5),
- Phenols separation (Figure 6),
- Cooling water air cooling system, and
- Storage (Figure 7).

In addition, three area samples will be taken on plant site.

Sections not included in sampling:

- Coal drier,
- Air decomposition,
- Biological water cleaning,
- Heating plant, and
- Water preparation.

Generator Section

The Generator Section (Figure 2) performs the gasification of coal according to the Lurgi process. The dried coal of class - 60 + 6 mm is fed by conveyor belts to the coal bin (1). In the bin, the coal is protected by nitrogen atmosphere. By the coal lock bucket (2) the coal is fed into coal lock (3) and further into generator (4). In the generator, the coal is gasified in the presence of stream and oxygen. The crude gas formed is lead first through the cooler with direct water injection (5), and then through two indirect coolers (6) and (7) and supplied to the Condensation Section. From the raw gas, condensates and high boiling points (tar) are separated in the coolers, as well as one part of the carried dust and contained water vapour. This tar gas liquor is fed into the gas liquor tank (15) and gas liquor gate (16) at start, i.e., directly to the tar separation section. The ash and a part of unreacted coal are discharged from the generator through the ash lock (9) and ash chamber (10) into the quenching bath, and then to the disposal area. Since the locks (3) and (9) are under pressure, their charging i.e., discharging requires partial

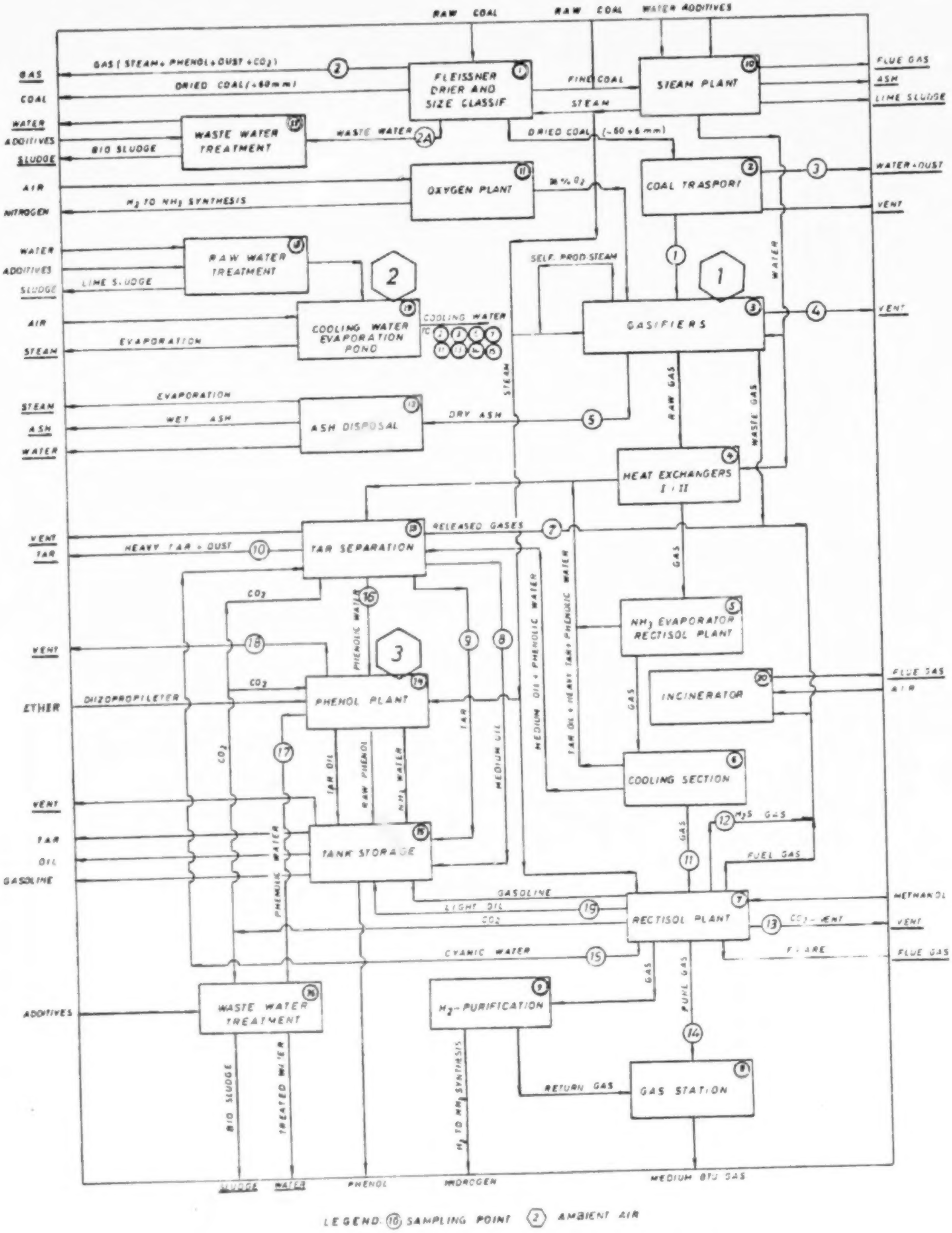

RAW COAL
RAW COAL
WATER ADDITIVES
GAS
COAL
WATER
ADDITIVES
SLUDGE
AIR
NITROGEN
WATER
ADDITIVES
SLUDGE
AIR
STEAM
STEAM
ASH
WATER
VENT
TAR
VENT
ETHER
VENT
TAR
OIL
GASOLINE
ADDITIVES
GAS (STEAM + PHENOL + DUST + CO2)
DRIED COAL (+60 mm)
FLEISSNER DRIER AND SIZE CLASSIF
FINE COAL
STEAM
STEAM PLANT
FLUE GAS
ASH
LIME SLUDGE
WASTE WATER TREATMENT
BIO SLUDGE
WASTE WATER
2A
DRIED COAL (-60 +6 mm)
OXYGEN PLANT
98 % O2
H2 TO NH3 SYNTHESIS
COAL TRASPORT
WATER + DUST
VENT
RAW WATER TREATMENT
LIME SLUDGE
SELF. PROD. STEAM
WATER
COOLING WATER EVAPORATION POND
EVAPORATION
COOLING WATER
TC
GASIFIERS
VENT
EVAPORATION
WET ASH
ASH DISPOSAL
DRY ASH
STEAM
RAW GAS
WASTE GAS
HEAT EXCHANGERS I + II
TAR SEPARATION
RELEASED GASES
HEAVY TAR + DUST
GAS
CO2
PHENOLIC WATER
NH3 EVAPORATOR RECTISOL PLANT
MEDIUM OIL + PHENOLIC WATER
TAR OIL + HEAVY TAR + PHENOLIC WATER
CO2
DIIZOPROPILETER
PHENOL PLANT
INCINERATOR
FLUE GAS
AIR
GAS
TAR
MEDIUM OIL
CO2
TAR OIL
RAW PHENOL
NH3 WATER
COOLING SECTION
PHENOLIC WATER
TANK STORAGE
GAS
H2S GAS
FUEL GAS
GASOLINE
LIGHT OIL
CO2
RECTISOL PLANT
METHANOL
CO2 - VENT
VENT
FLARE
FLUE GAS
CYANIC WATER
GAS
PURE GAS
WASTE WATER TREATMENT
H2 - PURIFICATION
BIO SLUDGE
TREATED WATER
H2 TO NH3 SYNTHESIS
RETURN GAS
GAS STATION
SLUDGE
WATER
PHENOL
HYDROGEN
MEDIUM BTU GAS
LEGEND: 10 SAMPLING POINT 2 AMBIENT AIR

Figure 1. Process flow diagram for gasification process in Remhk Kosovo.

TABLE 1

SAMPLE SCHEDULE

		Sample	Flow	Trace elements SSMS	Trace organics	GCMS	HPLC	AA	Particle size
1	Coal Feed	Composite	X	X	X	-	-	X	-
2	Coal drying - vent gases	F+C	-	X	X	X	-	-	X -grain loading only
2A	Coal drying - condensate	Composite	-	X	X	-	-	-	-
3	Coal bin vent gases	F+C	X	X	X	-	-	-	X
GASIFIER									
4	Low Raw Gas	F+C	X	X	X	-	-	-	X
5	Ash	Composite	X	X	X	-	-	X	-
QUENCH SYSTEM									
7	Gas to incinerator	F+C	$\boxed{X}$	-	X	X	-	-	-
8	Oil	Composite	X	X	X	X	-	X	-
9	Tar	Composite	X	X	X	X	X	X	-
10	Heavy tar + solids	Composite	X	X	X	X	X	X	-
11	Raw gas after cooler	F+C	$\boxed{X}$	X	X	X	X	X	X -grain loading only
RECTISOL									
12	H_2S vent gas	F+C	X	-	X	X	-	-	-
13	CO_2 vent gas	F+C	X	-	X	X	-	-	-
14	Clean gas	F+C	X	X	X	X	-	ⓧ	-
15	Condensate	Composite	X	X	X	X	-	-	-
19	Benzene/light oil	Composite	X	-	X	X	-	-	-
PHENOSOLVAN									
16	Inlet water	Composite	X	X	X	X	X	X	-
17	Outlet water	Composite	-	X	X	X	X	-	-
18	Vent	C	$\boxed{X}$	-	X	X	-	-	-

$\boxed{X}$ - If possible.

ⓧ - Particles shall be collected and analyzed only if particles are found in the product gas at Point 11.

F+C - Sampling train with filter and XAD-2 cartridge.

C - Cartridge only.

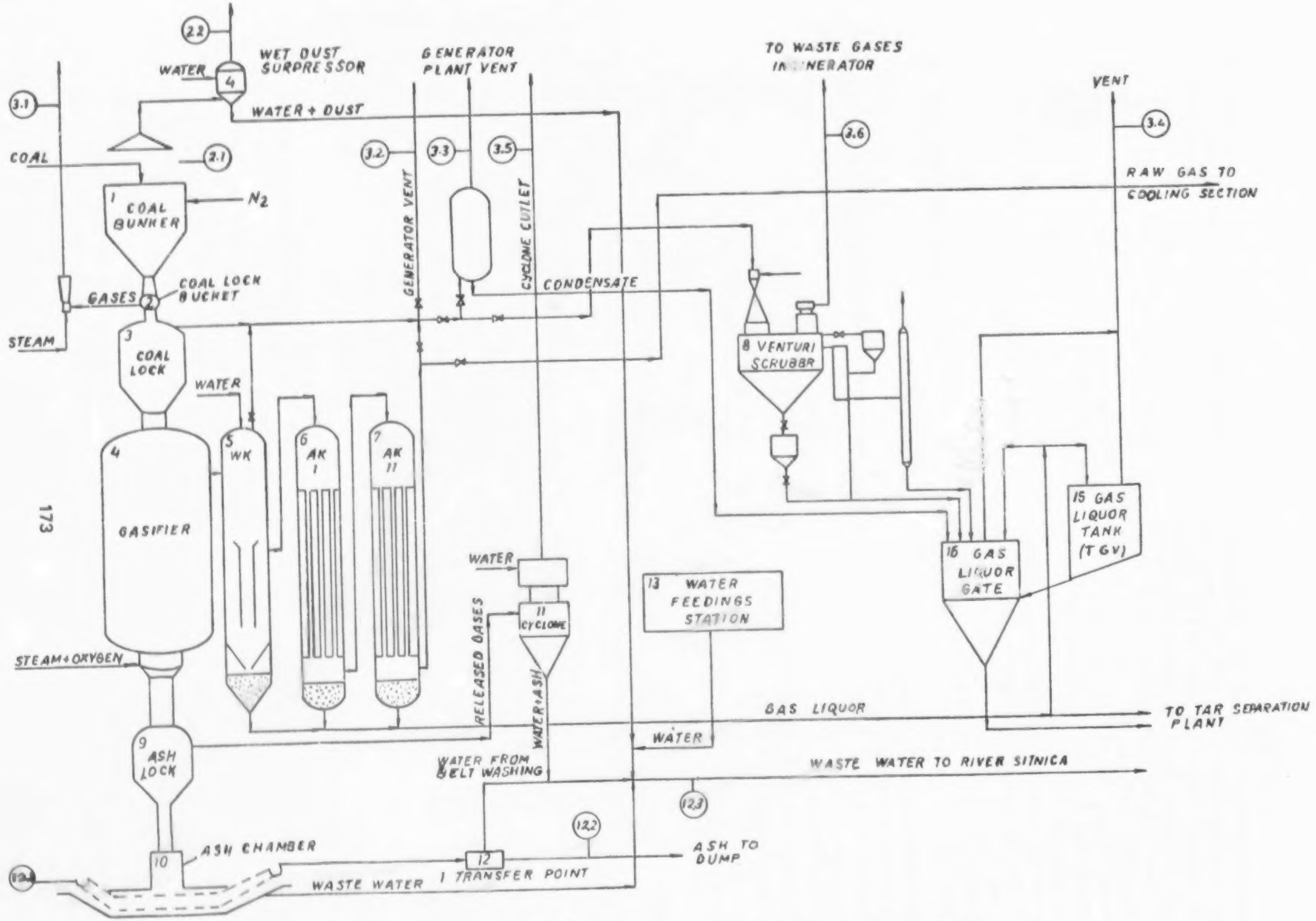

3.1
2.2
WATER
4
WET DUST
SURPRESSOR
WATER + DUST
GENERATOR
PLANT VENT
TO WASTE GASES
INCINERATOR
VENT
2.6
3.4
COAL
2.1
3.2
3.3
3.5
RAW GAS TO
COOLING SECTION
1 COAL
BUNKER
N2
GENERATOR VENT
CYCLONE CUTLET
CONDENSATE
COAL LOCK
BUCKET
GASES
2
STEAM
3 COAL
LOCK
8 VENTURI
SCRUBBR
WATER
4
5 WK
6 AK I
7 AK II
GASIFIER
15 GAS
LIQUOR
TANK
(T GV)
16 GAS
LIQUOR
GATE
WATER
13 WATER
FEEDINGS
STATION
RELEASED GASES
11 CYCLONE
STEAM+OXYGEN
WATER+ASH
GAS LIQUOR
TO TAR SEPARATION
PLANT
9 ASH
LOCK
WATER
WATER FROM
BELT WASHING
WASTE WATER TO RIVER SITNICA
12.3
12.2
ASH CHAMBER
10
12
ASH TO
DUMP
12.4
WASTE WATER
1 TRANSFER POINT

Figure 2. Process flow diagram and sampling points in generator plant.

decompression. During coal lock decompression, prior to charging with coal, the gases are lead through venturi scrubber (8) to waste gases incinerator (up to a pressure of about 2 atm), and then through generator vent (up to atmospheric pressure). Coal lock bucket decompression is carried out through a separate vent at each coal charge. Before ash discharge from the ash lock, decompression is carried out through wet dedusting cyclone (11). For the dedusting of transfer points during the feed of coal bunkers, a ventilation system is provided with wet dedusting of the suction gases in cyclone (14).

The wastewaters from cyclones (11), (14), ash quenching baths, belt washing at the I ash transfer point (12) and feed water station are collected in a common sump and delivered to the River Sitnica.

The grade of lignite - 60 + 6 mm, dried by "Fleissner" method, is as follows:

Proximate and ultimate analysis:

	Operating moisture	Operating moisture	Moisture free	Moisture & ash free
Moisture	26.62	22.0	–	–
Ash	14.78	17.71	20.14	–
S total	0.97	1.03	1.32	1.66
S bound	0.80	0.85	1.09	1.37
Coke	40.37	42.91	55.01	43.67
C fix	25.59	27.20	34.87	43.67
Volatiles	33.01	35.09	44.99	56.33
Combustibles	58.60	62.29	79.86	100.00
Heating value				
Gross Kcal/kg	3,647	3,877	4,970	6,223
Net, Kcal/kg	3,358	3,604	4,775	5,979
Carbon	40.17	42.70	54.74	68.55
Hydrogen	2.91	3.10	3.97	4.97
S combustion	0.17	0.18	0.23	0.29
N + O	15.35	16.31	20.92	26.19

Low-temperature carbonisation analysis according to Fischer at 520° C:

(Dried Kosovo lignite, size – 60 + 6 mm)

	%	%
Operating moisture	7.20*	–
Tar	5.82	6.27
Gas water	9.00	9.70
Semi coke	62.30	67.13
Gas + losses	15.68	16.90

*Partly dried sample.

Analysis of dried Kosovo lignite ash, size - 60 + 6 mm:

Analysis of dried Kosovo lignite ash, size –60+6 mm:

Components	**%**
SiO_2	25.01
Fe_2O_3	6.84
Al_2O_3	6.73
CaO	36.03
MgO	6.33
SO_3	16.13
P_2O_5	0.34
TiO_2	0.51
Na_2O	1.58
K_2O	0.40
MnO	0.14

Base-to-acid ratio = 1.58
$Fe_2O_3/CaO = 0.18$

Ash fusibility:

(oxidative atmosphere)

Initiation of sintering	970° C
Softening temperature	1130° C
Hemisphere temperature	1290° C
Flow temperature	1300° C

Each generator unit consists of six generator vessels, 1, 2 through 7, 9, and 10, an ash bath, vents of coal lock buckets and generator vents, two dedusting cyclones 14 and one vessel 8, 15, 16, 11, one ash transfer point, one feed water station and one generator section vent (forced expansion vent).

The research program includes determinations of the composition of gases from:

- Coal lock bucket vent (3.1)

- Dedusting cyclones (2.2)
- Generator vents (3.2)
- Generator section vent (3.3)
- Ash lock expander cyclone (3.5)
- Tar gas water vent (3.4) and gases to waste gas incinerator (3.6).

Pollution determinations will also be made for coal supply rooms (2.1) and the surroundings of uncomplete ash lock decompression (12.1). In addition, determinations will be made of the amount and composition of ash (12.2), and quality of wastewater from the generator section (12.3).

Information on the sampling points in the plant is given below.

Sampling points - Section Generators

1. Sampling point No. (2.1): in coal supply room:
    - major pollutants: escaped dust and possibly gases form coal bunker,
    - cause of pollution: supply of finer coal fractions and insufficient efficacious dust removal system from critical points,
    - measurement magnitudes: dust content in the air and air analysis,
    - measuring points: transfer point on level 37 m, transfer point on level 35 m.

Note: Periodically pollution is very high.

2. Measurement point No. (2.2): Dedusting cyclone discharge into the atmosphere:
    - major pollutants: as under item 1,
    - cause of pollution: insufficient efficacious dedusting and possible escaped gases from the generators,
    - measurement point: on fan house roof, two fans, discharge tube Dia 1500 mm, and
    - measurement magnitudes: dust concentration and air analysis.

Note: Current system of six united and connected suction points on a single fan insufficiently efficacious, resulting in low discharge into the atmosphere.

3. Measurement point No. (3.1): coal lock bucket decompression:
    - major pollutants: water vapour, gases from generators, and coal dust,
    - cause of pollution: technological solution of discharging the gases into the atmosphere,
    - measurement point: outlet into the atmosphere designed on building roof, but current outlet on level 25 away from the building on the platform. Sampling point pipe Dia 3''. Steam discharged under pressure.
4. Measurement point No. (3.2): Generator vent (small flare):
    - major pollutants: flue gases upon treatment inclusive cooler AK II 2 h after start, gases from generators during coal lock expansion from 2 kp/cm^2 to atmospheric pressure and flue gases upon generator extinquishing (burning out after water vapour action in absence of air or oxygen about 24 h after shut down), gases from coal lock during every coal charging,
    - measurement point: outlet into the atmosphere on generator section roof, but more suitable sampling point on level 25 in pipe straight run, requiring fitting.
5. Measurement point No. (3.3): Generator Section vent (large flare):
    - major pollutants: gases from generator during startup feeding the first amount of coal into the generator and until pressure reaches 6 atm. (up to 7 days), and waste gases from tar gas liquor tank into which the condensed products are returned collecting all spoiled waters from the Generator Section,
    - cause of pollution: technological solution of discharging the gases into the atmosphere,
    - measurement point: platform on level 35 m outdoors, and
    - measurement magnitude: gas composition.

Note: According to the design, the Generator Section vent is used for all the six generators and collects all other gases from leaking valves.

6. Measurement point No. (3.4): Vent

from tar gas liquor and all Generator Section waste waters tanks:

- major pollutants: phenols and higher hydrocarbons, H_2S,
- cause of pollution: technological solution of discharging the gases into the atmosphere, and
- measurement point: on Generator Section roof (unsuitable) or TGV outlet.

7. Measurement point No. (3.5): Vent from lock expander cyclone:
   - major pollutants: gases from ash lock expander and finer ash,
   - cause of pollution: technological solution providing the discharge of ash lock expander cyclone into the atmosphere,
   - measurement point: on Generator Section roof, or outlet of cyclone on 9 m level, and
   - measurement magnitudes: gas composition.

Note: Technological design provides one expander for six ash locks with cyclone dedusting.

8. Measurement point No. (3.6): Coal lock expansion gases— major pollutants: generator gas during start (above 6 atm) and gases from coal lock during expansion to 2 atm:
   - measurement point: ahead of venturi scrubber, and
   - measurement magnitude: gas composition.
9. Measurement point No. (12.1): Pollution due to incomplete ash lock decompression:
   - major pollutants: gases from ash lock and ash,
   - cause of pollution: inadequate solution of the system for ash lock pressure control,
   - measurement point: ash quenching bath, level 0, and
   - measurement magnitude: gas composition and ash content in the gas.
10. Generator Section wastewaters (12.3): water from ash quenching baths, dedusting cyclones, expander cyclones, ash lock, ash belt washing water at I transfer point and cleaned water from fire hydrant system are combined in a very unsuitable sump, so that wastewaters' quantity determination is impossible, but the quality may be determined quite readily.
11. Gasification slag (12.2): Measurement of the amount of slag may be performed by removing from the belts or at the first transfer point, when sampling can be made.

Gas composition at AK II outlet

CO_2	29 - 32 vol. - %
H_2S	0.6 vol. - %
C_mH_n	0.75 vol. - %
CO	12 - 15 vol. - %
H_2	40 - 42 vol. - %
N_2	3 vol. - %
O_2	0.25 vol. - %
NH_3	5 - 7 g/100 Nm^3 on dry basis
NCH	5 - 7 g/100 Nm^3 on dry basis
S_{org}	20 g/100 Nm^3 on dry basis
Gasoline	7 g/100 Nm^3 on dry basis
Tar	21 - 25 g/100 Nm^3 on dry basis
Medium oil	18 - 20 g/100 Nm^3 on dry basis
Dust	0.1 g/100 Nm^3 on dry basis
Water	400 - 500 g/100 Nm^3 on dry basis

Condensation Section

In the Condensation Section, Figure 3, cooling and cleaning of the generator gas takes place. The section consists of three identical units, each containing a tar separator, four parallel countercurrent coolers, and a drop separator. The gas is further fed to the Rectisol Section, while the two separated intermediate products are supplied for tar, i.e., medium oil extraction.

According to the technological flowsheet there is no direct environmental

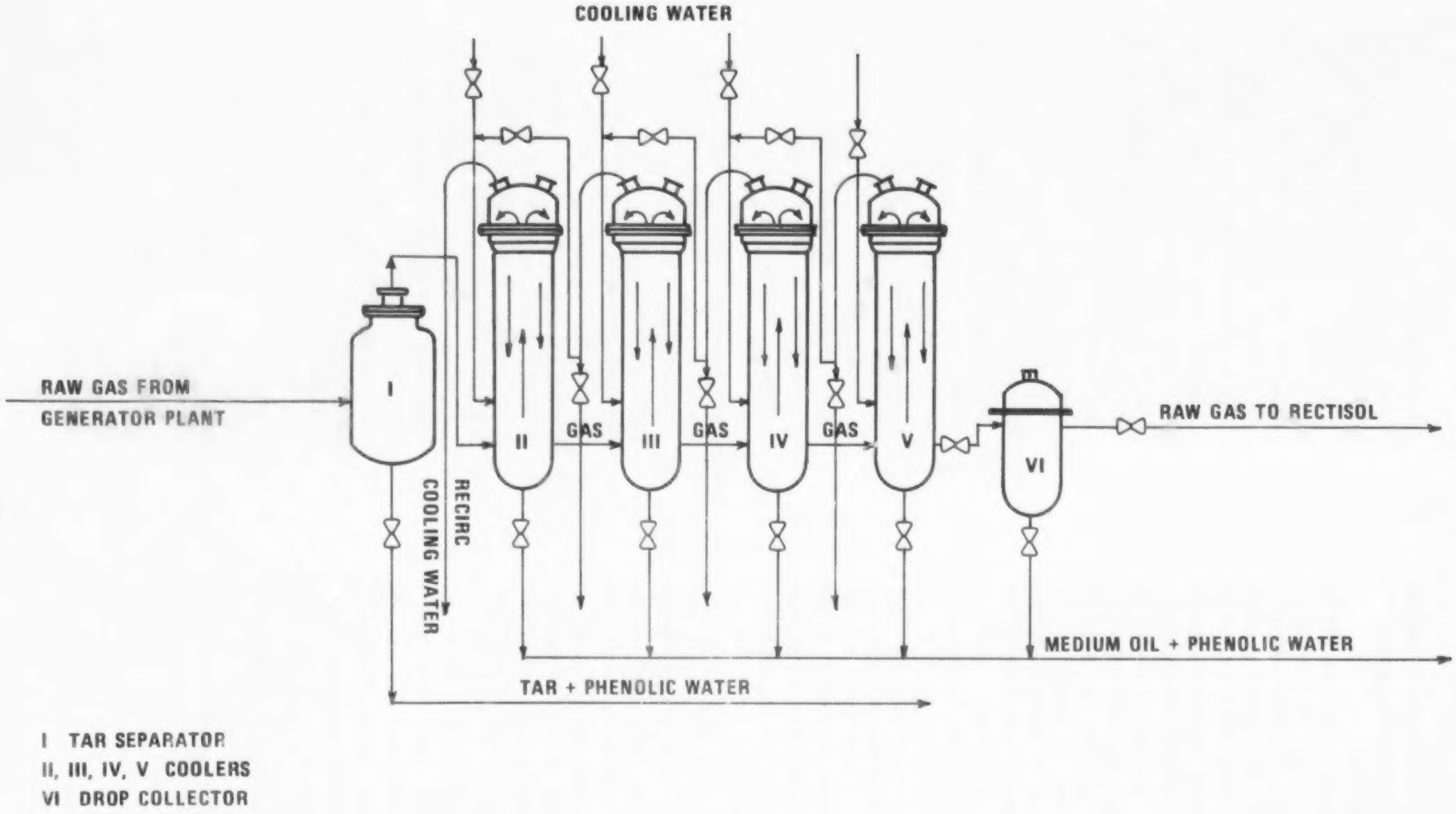

COOLING WATER
RAW GAS FROM
GENERATOR PLANT
I
II
III
IV
V
VI
GAS
GAS
GAS
RECIRC
COOLING WATER
RAW GAS TO RECTISOL
MEDIUM OIL + PHENOLIC WATER
TAR + PHENOLIC WATER
I TAR SEPARATOR
II, III, IV, V COOLERS
VI DROP COLLECTOR

Figure 3. Cooling section process flow diagram

pollution, except in the case of natural expansions and possible leakages.

Tar Separation Section

In the Tar Separation Section, Figure 4, liquid products from the Generator, Condensation, and Rectisol sections are separated. Tar and phenolic water of high pressure (from WK, AK I, and AK II) flow through preexpander (1) and expander (2) into the tar separator (3), while the other waters, including the cyanidic water from Rectisol Section, are fed directly to the tar separator. From the tar separator, the lightest tar fraction is delivered to the tar tank (4). In case of the inflow of impure fractions, a "slop" tank is available - impure tar tank (5), primarily used for recirculation to the tar separator. The medium fraction -phenolic water is fed into two phenolic water tanks (6), and then to the Phenosolvan Section. If required, a part of the liquid from phenolic water tank may be recycled to the tar separator through the impure tar tank. For the removal of heavy tar containing dust from tar separator, a surge tank (7), mixer tank (8) and mixture tank (9) are provided, but since this fraction is still not used for gasification in the generators, the heavy tar and dust are discharged directly through a bypass, loaded into a cistern and disposed outside the Kombinat grounds. The expansion gases from units 1, 2, 3, and 12 are passed through cooler (10) to the point of combining with other waste gases from the Generator Section and lead to the waste gases incinerator. The cooler condensate gas liquor is collected in a separate tank (12) and then treated in medium oil separator (12) (two units are available). This separator also collects the medium oil and phenolic water condensation products from the Condensation Section, and gas liquor from the Rectisol Section. From the medium oil separator the oil is delivered to medium oil tank (13), and the phenolic water to the phenolic water tanks.

In the case of emergency, a "slop" tank for impure oil (14) is available, and its content may be supplied to tar separator or to the storage. The tanks (4), (5), (6), (11), (13), and (14) are connected with the atmosphere by vents, so the program of activities envisages the determination of discharges composition. In addition to above samples, the composition of expansion gases ahead of coller (10) will be determined as well as the amount of heavy tar.

Data on sampling points in this Section follow below:

Sampling Points - Tar Separation Section

Tar separation section major pollutants are higher hydrocarbons, volatile phenols, and H_2S.

The cause of pollution is the technological solution providing the connection of all units by vents with the atmosphere.

Measurement magnitude: gas composition

1. Measuring point No. (13.1): Tar tanks (4) on Figure 4 - measurement point: vents on level 0, Dia 50 mm.
2. Measuring point No. (13.2): Impure tar tank (5) on Figure 4.
3. Measuring point No. (13.3): Medium oil tank (13) on Figure 4 - measurement point: vent on level 0, pipe Dia 50 mm.
4. Measuring point No. (13.4): Impure oil tank (14) on Figure 4 - measurement point: vent on platform on level 3 m, pipe Dia 150 mm.
5. Measuring point No. (13.5): Gas condensate tank (11) on Figure 4 -measurement point: vent on level 0, pipe Dia 50 mm.
6. Measuring point No. (13.6): Expansion gases to waste gases incinerator -measurement points: valve on the bend before combining with expansion gases from the generators, level 5 m, pipe Dia 100 mm.
7. Measuring point No. (13.7): Phenolic water tanks (two) - measurement

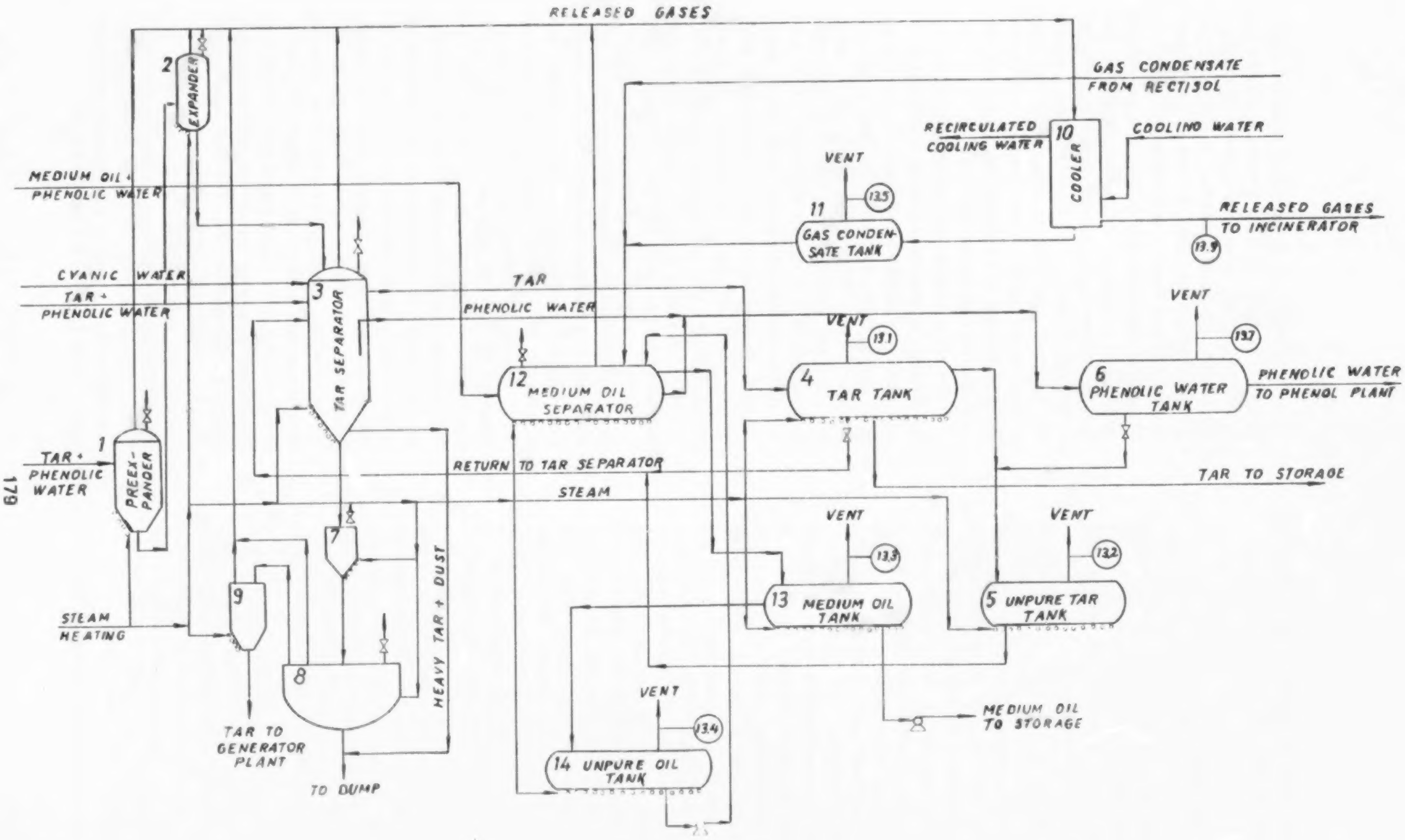

RELEASED GASES
GAS CONDENSATE
FROM RECTISOL
RECIRCULATED
COOLING WATER
10
COOLER
COOLING WATER
RELEASED GASES
TO INCINERATOR
13.9
2
EXPANDER
MEDIUM OIL +
PHENOLIC WATER
VENT
13.5
11
GAS CONDEN-
SATE TANK
CYANIC WATER
TAR +
PHENOLIC WATER
3
TAR SEPARATOR
TAR
PHENOLIC WATER
VENT
13.1
VENT
13.7
12
MEDIUM OIL
SEPARATOR
4
TAR TANK
6
PHENOLIC WATER
TANK
PHENOLIC WATER
TO PHENOL PLANT
TAR +
PHENOLIC
WATER
1
PREEX-
PANDER
RETURN TO TAR SEPARATOR
STEAM
TAR TO STORAGE
VENT
13.3
VENT
13.2
7
HEAVY TAR + DUST
9
STEAM
HEATING
13
MEDIUM OIL
TANK
5
UNPURE TAR
TANK
8
TAR TO
GENERATOR
PLANT
TO DUMP
VENT
13.4
14
UNPURE OIL
TANK
MEDIUM OIL
TO STORAGE

Figure 4. Process flow diagram and sampling points in tar separation plant.

point: vent on platform on level 3 m, pipe Dia 150 mm.

RECTISOL SECTION

The Rectisol Section (Figure 5) performs gas cleaning with water and methanol primarily from gasoline, CO_2 and H_2S, as well as the regeneration of spent methanol.

The gas delivered from the Condensation section passes through the drop separator (1) and flows into first stage gas cooling in the bottom section of column (2). According to the design, the gas should be washed with a mixture of gasoline and water, but currently only cold water is used. From the bottom section of column (2), the gas flows to the second cooling stage with methanol and purified gases in cooler (3) and column (2) upper section. Methanol with gas condensates from the lower part of column (2) upper section serve as the cooling and antifreezing agent in cooler (3) where the clean gas is heated. The cooling methanol for column (2) upper section comes from the bottom of column (5). The cooled gas freed of gasoline is fed for further cleaning (primarily from H_2S) to column (4). The methanol for above washing also comes from the bottom of column (5). Further gas cleaning develops in column (5) primarily of CO_2. The methanol for cleaning in column (5) comes from the bottom of regeneration column (14), i.e., from the bottom of the fourth stage of regeneration column (15) and the bottom of column (6). The clean medium heating value gas may be delivered from column (5) to the gas station being previously heated in heat exchanger (3), or fed for purification in column (6). The methanol for gas purification in column (6) is freshly added, or supplied from the bottom of column (14) and the fourth stage of column (15).

The water containing gasoline from the lower part bottom of column (2) is fed to separator (7), and the gasoline is delivered through tank (8) to the storage, and the water together with cyanic water to the tar separation section. The expansion gases from separator (7) are lead to the collection line of rich waste gases.

The methanol containing gasoline from the bottom of heat exchanger (3) is supplied to expander (9) and then to extractor (10). The gasoline fraction is separated from the water-methanol solution in the extractor. The gasoline is fed to tank (8) and the methanol water solution first to distillation column (11) to remove the residual gasoline, and then to the rectification column (12) to separate the methanol from water. Stripping nitrogen is fed to the top of column (12), and NaOH through the bottom primarily to neutralize the free hydrocyanic acid. The impure methanol vapours are fed to expander (9), and the clean methanol fumes to column (14).

The methanol from the bottom of column (4) is supplied to column (13) for regeneration in succession to stages I, II, III, and IV. The expansion gases from column (13) first stage are combined with those in the rich waste gases line, and the waste gases from the remaining stages into the common H_2S gases line. Into the upper section of column (13) fourth stage the gas-released waste gas in column (14) is included. The methanol from column (13) fourth stage bottom, the condensed methanol from column (14) waste gases and water vapour and methanol fumes from the top of column (12) are fed to column (14). The purified methanol from the bottom of column (14) serves for gas cleaning in columns (6) and (5). The waste gases from column (14) are fed the upper part of column (13) fourth stage. The methanol from column (5) bottom is partially supplied to columns (2) and (4), and partially to regeneration column (15). Column (15) is divided into four stages, and the methanol passes through all the stages in succession. The expansion gases from column (15) first section are lead to the common rich waste gases line. The waste gases from remaining stages are combined and fed to the CO_2 waste gases vent. The amount of above waste gases may be obtained by summation of the amounts of gases from FR 39 and measured amounts at fitted measurement points FE 33 and FE 28. The rich waste gas amount consisting of expansion gases from column (9), separator (7) and first stages of columns (13) and (15) may be read on recorder FR 27. The amount of H_2S waste gas may be determined by summing the measurements at fitted points FE 21, FE 22, and FE 23.

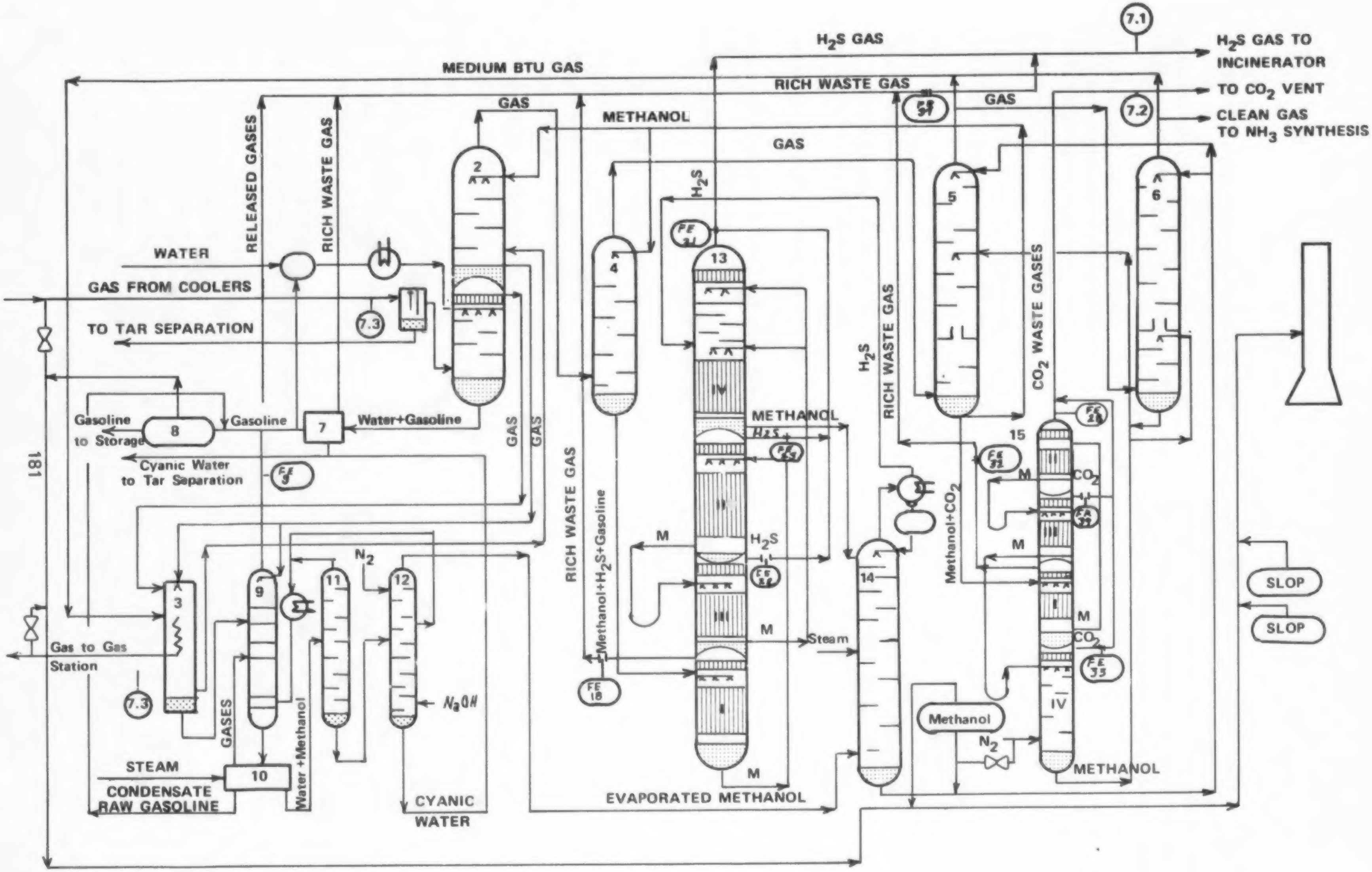

H$_2$S GAS
MEDIUM BTU GAS
RICH WASTE GAS
(7.1)
H$_2$S GAS TO INCINERATOR
TO CO$_2$ VENT
(7.2)
CLEAN GAS TO NH$_3$ SYNTHESIS
GAS
METHANOL
RELEASED GASES
RICH WASTE GAS
WATER
GAS FROM COOLERS
TO TAR SEPARATION
(7.3)
Gasoline to Storage
Gasoline
Water+Gasoline
Cyanic Water to Tar Separation
FE 9
Gas to Gas Station
STEAM
CONDENSATE
RAW GASOLINE
GASES
Water +Methanol
N$_2$
NaOH
CYANIC WATER
RICH WASTE GAS
Methanol+H$_2$S+Gasoline
FE 18
H$_2$S
FE 21
METHANOL
H$_2$S
M
Steam
EVAPORATED METHANOL
CO$_2$ WASTE GASES
Methanol+CO$_2$
FE 32
FE 28
FE 35
CO$_2$
Methanol
METHANOL
SLOP
SLOP
2
3
4
5
6
7
8
9
10
11
12
13
14
15
I
II
III
IV

Figure 5. Process flow diagram and sampling points in Rectisol plant.

Having in view that the lines of rich waste gas and waste H_2S gas are combined and lead to the waste gases incinerator, their amount may be obtained by summing individual gas streams. The program of activities provides for the determination of the quality of inlet and outlet gases of Rectisol Section, CO_2 waste gases, H_2S waste gases, and waste gases under Rectisol Section incinerator.

Sampling points data are as follows:

Sampling Points--Rectisol Section

1. Measurement point No. (7.1): H_2S waste gas:
   - major pollutants: H_2S, methane,and other hydrocarbons,
   - cause of pollution: technological solution providing combustion of the gases by waste gases incinerator before discharge into the atmosphere,
   - measurement magnitudes: gas composition and volume, and
   - measuring point: methanol recycle line at E4/5, level 0, connection line on valve dia 8 for analysis. The amount of gases obtainable by summing the amounts of gases measured at fitted measurement points FE 23, FE 22, and FE 21. Platforms available on level 10 for mounting the measurement instruments.
2. Measurement point No. (7.2): CO_2 - vent line:
   - major pollutants: in addition to CO_2, methanol, H_2S and higher hydrocarbons may be present,
   - cause of pollution: direct discharge of the gases into the atmosphere,
   - measurement magnitudes: gas composition and amount,
   - measuring points: analysis sample at G5, Dia 10 mm. The amount of gases obtainable by summing the values measured at fitted measuring points FE 28, FE 33, or by measuring the total amount by a Pitot tube in the line at G5, dia.1000, level 0 (fitting required).
3. Measurement point No. (7.3): Rectisol Section incinerator:
   - major pollutants: during proper incinerator operation no pollutants should be generated,
   - cause of pollution: technological solution provided burning the gases from generators if Rectisol Section out of operation, or cleaned gases if further gas transport prevented, burning of evaporates from gasoline, methanol, and two "slop" tanks,
   - measuring points: (when incinerator unoperative) gas at rectisol inlet - sample at PRCX, dia. 10, i.e., clean gas at E1, dia. 10, i.e., methanol and benzene fumes, and
   - measurement magnitude: gas composition.

The Rectisol Section has no direct discharges of waters into the surroundings.

Expected H_2S waste gases composition at measurement point 7.1.

CO_2	57.25 - 49.75 vol. - % i.e.	37 - 88 vol. - %
C_mH_n	0.575 - 0.675 vol. - % i.e.	0.5 - 1.2 vol. - %
O_2	0.175 - 0.3 vol. - % i.e.	0.1 - 0.3 vol. - %
CO	3.225 - 7.050 vol. - % i.e.	0.9 - 7.2 vol. - %
H_2	18.35 - 36.9 vol. - % i.e.	1.4 - 39.6 vol. - %
CH_4	9.45 - 15.6 vol. - % i.e.	6.6 - 15.6 vol. - %
N_2	1.8 - 2.2 vol. - % i.e.	1.8 - 2.2 vol. - %
H_2S	1,034 - 629 g/100 Nm^3	682 - 1,920 g/100 Nm^3
NHV	2,170 - 2,252 $Kcal/Nm^3$	970 - 2,680 $Kcal/Nm^3$

Expected composition of gases to CO_2 vent at measurement point 7.2.

CO_2	54 - 86 vol. - %
C_mH_n	0.4 - 1 vol. - %
O_2	0.1 - 0.3 vol. - %
CO	6.6 - 2.8 vol. - %
H_2	19.8 - 3.8 vol. - %

CH_4	17.4 - 6.7 vol. - %
N_2	2.8 - 0.2 vol. - %
H_2S	400 - 1,200 g/100 Nm^3

Designed composition of the gas at Rectisol Section inlet: measurement point 7.3.

CO_2	29 - 86 vol. - %
H_2S	0.60 vol. - %
C_mH_n	0.75 vol. - %
CO	12 - 15 vol. - %
H_2	40 - 42 vol. - %
CH_4	11 - 13 vol. - %
N_2	3 vol. - %
O_2	0,35 vol. %
NH_3	5 - 7 g/100 Nm^3
HCN	5 - 7 g/100 Nm^3
S	20 g/100 Nm^3
Gasoline	7 g/Nm^3
Medium oil	2 g/Nm^3
Dust	0.1 g/Nm^3
Water	1.3 - 1.4 g/Nm^3

Designed quality of pipeline gas at measurement point 7.3.

CO_2	2.0 vol. - %
H_2S	2.0 vol. - ppm
CH_4	16.1 vol. - %
C_mH_n	0.5 vol. - %
CO	19.4 vol. - %
H_2	58.2 vol. - %
N_2	3.8 vol. - %
NHV	3,800 Kcal/Nm^3

Expected composition of gases from expander (7) and separator (7) combined:

CO_2	approx. 61 - 37 vol. - %
H_2	approx. 24 - 39.6 vol. - %
CH_4	approx. 10.4 - 15.6 vol. - %
C_mH_n	approx. 0.6 - 0,5 vol. - %
O_2	approx. 0.2 - 0.3 vol. - %
CO	approx. 4 - 7.2 vol. - %
H_2S	1,100 - 682 g/100 Nm^3
NHV	approx. 2,000 - 2,680 Kcal/Nm^3

Expected composition of gases from column (13) and column (15) first stage:

CO_2	46 - 88 vol. - %
C_mH_n	0.5 - 1.2 vol. - %
O_2	0.1 - 0.3 vol. - %
CO	0.9 - 6.6 vol. - %
H_2	1.4 - 28.8 vol. - %
CH_4	6.6 - 15.6 vol. - %
N_2	1.8 - 2.2 vol. - %
H_2S	835 - 1,910 g/100 Nm^3
NHV	2,680 - 970 Kcal/Nm^3

PHENOSOLVAN SECTION

The Phenosolvan Section (Figure 6) serves primarily for the removal of a major part of phenol from phenolic waste water prior to final biological treatment. According to the design, butylacetate should be used as the extracting agent, but currently diisopropylether is used in REMHK Kosovo for phenol extraction.

The phenolic water is fed into cyclone (1) for treatment with CO_2 (currently no CO_2 injection) and then passed to tank (2) for the separation of residual oil and tar from phenolic water. The impure oil is delivered through tank (3) to the storage, while the tar is directly fed to the Tar Separation Section. The phenolic water is supplied through sand filters (4) to two surge tanks (5) and then upon heating in heat exchanger (6) to degasing column (7). Reheating of phenolic water takes place in column (7) lower section. Prior to entering column (9) upper section,

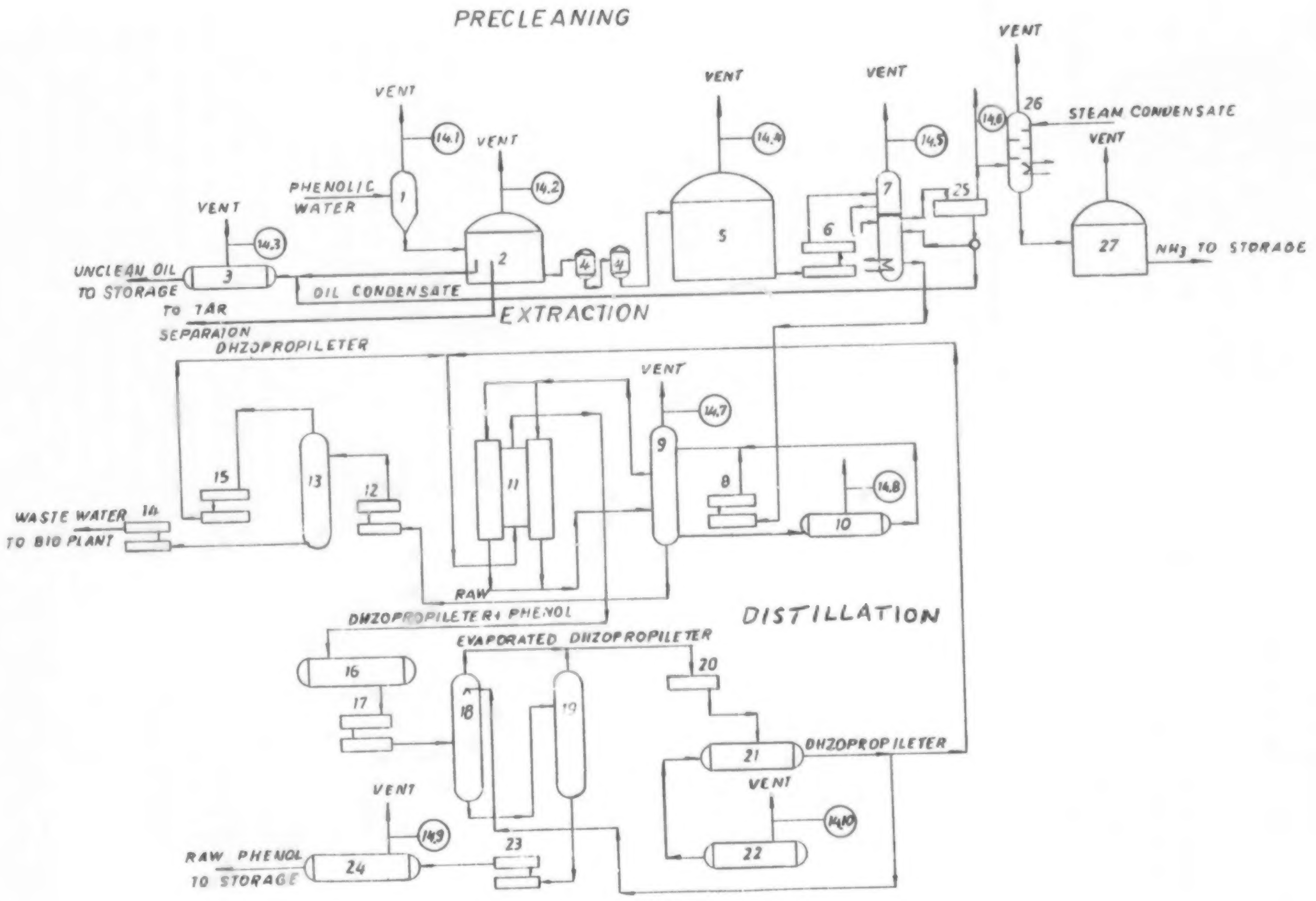

PRECLEANING
EXTRACTION
DISTILLATION
VENT
14.1
14.2
14.3
14.4
14.5
14.6
14.7
14.8
14.9
14.10
PHENOLIC WATER
UNCLEAN OIL TO STORAGE
TO TAR SEPARAION
OIL CONDENSATE
DHZOPROPILETER
STEAM CONDENSATE
NH3 TO STORAGE
WASTE WATER TO BIO PLANT
RAW DHZOPROPILETER + PHENOL
EVAPORATED DHZOPROPILETER
RAW PHENOL TO STORAGE
1
2
3
4
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27

Figure 6. Process flow diagram and sampling points in Phenosolvan plant.

where additional gases release is completed, the phenolic water is cooled in cooler (8). The phenolic water from "slop" tank (10) is also fed to column (9) upper section. The cold phenolic water, free of gases, is fed for extraction to extractors (11), and then to heat exchanger (12) for heating and distillation from conveyed diisopropilether in distillation column (13). From column (13) the cleaned phenolic water is delivered through cooler (14) to the section for biological waste waters treatment. The diisopropilether fumes are condensed in cooler (15) and fed combined with the diisopropilether from surge tank (21) to the extractor. The raw phenol extracted in diisopropilether is supplied through surge tank (16) for heating in heat exchanger (17) and then to rectification columns (18) and (19). The diisopropilether fumes are condensed in cooler (20). The condensed and fresh diisopropilether supplied from tank (22) are fed to tank (21) and supplied to the extractor. The raw phenol from the bottom of rectification column (1) is delivered through cooler (23) and tank (24) to the storage.

The gases from column (7) lower section are partially condensed in cooler (25) and ammonium fumes in column (26). Tank (27) is provided for aqueous ammonium solution. Currently, units (26) and (27) are inoperative and a water vent was fitted between units (25) and (26). Condensate water fraction is recycled to column (7) lower section, and the oil one to tank (3). Units 1, 2, 3, 5, 7 (upper section) directly and the lower one through coller (25), (9) (upper section), 10, 22 and 24 are connected by vents with the atmosphere, and our program of activities envisages the determination of discharge gases composition.

Information on section sampling points:

Sampling Points--Phenosolvan Section

- Cause of pollution: technological solution providing the discharge of the gases into the atmosphere through separate vents.

1. Measurement point No. (14.1): Cyclone vent (Figure 6):
   - major pollutant: phenol fumes,
   - measuring point: cyclone vent at top of K2, and
   - measurement magnitude: gas composition.
2. Measurement point No. (14.2): gas liquor tank (Figure 6) separation of tar, oil, and phenolic water:
   - major pollutants: phenol, oil, tar, and ammonium evaporations,
   - measuring point: tank roof lid, Dia. 500 mm, and
   - measurement magnitude: gas composition.
3. Measurement point No. (14.3): Impure oil tank (Figure 6):
   - major pollutant: oil evaporations including H_2S,
   - measuring point: filling funnel, level 0, Dia. 200 mm, and
   - measurement magnitude: gas composition.
4. Measurement point No. (14.4): Phenolic water tank (Figure 6):
   - major pollutant: volatile phenols,
   - measuring point: lid on tank roof, dia. 500 mm.
5. Measurement point No. (14.5): column vent (Figure 6):
   - major pollutants: ammonium, H_2S phenols,
   - measuring point: vent on column top, dia. 250 mm, and
   - measurement magnitude: gas composition.

Note: The amount of gaseous products is also determinable from the material balance on the basis of water composition. According to our free assessment, column K1 vent is the major pollutant of Phenosolvan Section.

6. Measurement point No. (14.6): vent (Figure 6 between 25 and 26):
   - major pollutant: ammonium fumes,
   - measuring point: vent at section top, dia. 50 mm, and
   - measurement magnitude: gas composition.
7. Measurement point No. (14.7): column vent (Figure 6):
   - major pollutants: similar as at K1,
   - measuring point: vent on column top, dia. 250 mm, and

- measurement magnitude: gas composition.

8. Measurement point No. (14.8): Phenosolvan Section waste waters tank (Figure 6/10):
   - major pollutants: volatile matter of oil, tar and phenol,
   - measuring point: vent on level 0, dia. 3", and
   - measurement magnitude: gas composition.
9. Measurement point No. (14.9): raw phenol tank (two units) (Figure 6/24):
   - major pollutants: phenol fumes,
   - measuring point: lid on tank roof, dia. 500 mm, and
   - measurement magnitude: gas composition.
10. Measurement point No. (14.10): diisopropilether tank (Figure 6/22):
    - major pollutant: diisopropileher fumes,
    - measuring point: tank vent, level 0, dia. 3", and
    - measurement magnitude: gas composition.

According to the design, the Phenosolvan Section has no discharge into the sewage system.

Note: The section for biological waste waters treatment is inoperative. The amount of water currently discharged directly into River Sitnica stream is measurable at the inlet into aeration pools. (Attention to be paid to the amount of diisopropilether.)

STORAGE

The storage, Figure 7, consists of seven tanks and a pump station. The gasoline, tar, impure and medium oil may be used for the mixture for burning supplied to the Power Generation Plant via a pipeline, or individually supplied for shipment. All tanks are connected with the atmosphere directly by vents, and the program provided the determination of discharge gases composition.

Phenol is stored in the ammonium tank, and other changes are also made as required.

Approximate composition of medium oil:

– water content	0.5 - 1.5%
– creosates content	28 - 32%
– paraffine content	0.3%
– naphatalene content	2 - 3%
– NHV	8,500 - 8,700 Coal/kg

Approximate composition of tar:

– asphalt content	13 - 23%
– paraffine content	3 - 4%
– creosate content	26 - 32%
– NHV	8,500 - 8,600 Coal/kg

Sampling points data follow below:

Sampling Points--Storage

1. Measurement point No. (15.1): vent on tar tank (two units):
   - cause of pollution: designed connection with the atmosphere by vents,
   - major pollutants: H_2 higher hydrocarbons,
   - measuring point: lid on tank roof, dia. 500 mm, and
   - measurement magnitude: gas composition.
2. Measurement points No. (15.2) and (15.5): vents on medium oil tanks (two units):
   - cause of pollution: designed connection with atmosphere by separate vents,
   - measuring point: lids on tank roofs, dia. 500 mm,
   - measurement magnitude: gas composition, and
   - major pollutants: medium oil fumes, H_2S.
3. Measurement point No. (15.3): Gasoline tank:
   - cause of pollution: designed discharge directly into the atmosphere,
   - major pollutants: highly evaporable gasoline fractions,
   - measuring point: lid on tank roof, dia. 500 mm, and

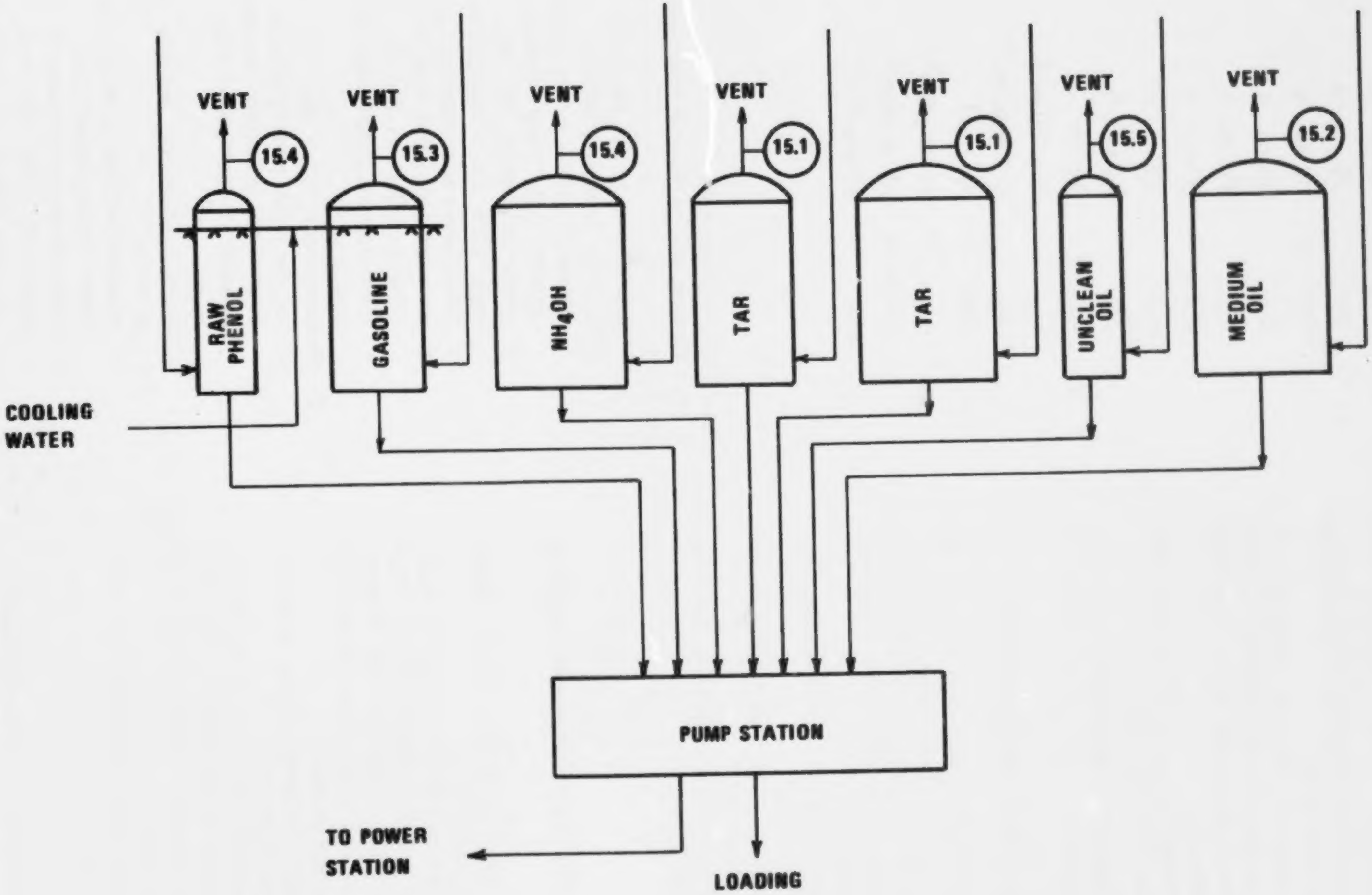

VENT
15.4
RAW PHENOL
VENT
15.3
GASOLINE
VENT
15.4
NH_4OH
VENT
15.1
TAR
VENT
15.1
TAR
VENT
15.5
UNCLEAN OIL
VENT
15.2
MEDIUM OIL
COOLING WATER
PUMP STATION
TO POWER STATION
LOADING

Figure 7. Process flow diagram and sampling points in storage.

    - measuring magnitude: gas composition.
4. Measurement point No. (15.4): Phenol tanks (two units):
    - cause of pollution: designed connection with atmosphere by vents,
    - major pollutants: highly evaporable phenols,
    - measuring point: lid on tank roof, dia. 500 mm, and
    - measuring magnitude: gas composition.

Cooling Water Coolers--Sampling Points

1. Measurement point No. (19.1): air discharge from the coolers:
    - cause of pollution: leakage from exchangers in gasification plant sections,
    - major pollutants: evaporable components,
    - measuring point: air outlet from the coolers, and
    - measurement magnitude: gas composition.

Expansion Gases Main Incinerator--Sampling Points

1. Measurement point No. (20.1): Gases to main incinerator:
    - cause of pollution: designed burning of expansion gases from Generation Section, Tar Separation, and H_2S waste gases from Rectisol Section,
    - major pollutants: higher hydrocarbons, H_2S (SO_2),
    - measuring point: line before the incinerator at the location of condensate separation, level 0, incinerator inlet, and
    - measurement magnitude: gas composition.

Expected composition of expansion gases at incinerator:

CO_2	40 vol. - %
H_2	35 vol. - %
CO	12 vol. - %
CH_4	10 vol. - %
N_2	2.5 vol. - %
C_mH_n	0.7 vol. - %
H_2S	0.6 vol. - %
O_2	0.2 vol. - %
Gasoline	7 g/Nm^3
S_{org}	20 g/100 Nm^3
NH_3	5 - 7 g/100 Nm^3
Water	70 g/Nm^3
Tar	21 - 25 g/Nm^3
Medium oil	18 - 20 g/Nm^3
Dust	0.1 g/Nm^3

Area Samples (Figure 1)

Area samples will be taken at three points on plant site:

1. Measurement point No. (1): Area around the Generator Section:
    - cause of pollution: gas production according to "Lurgi" procedure,
    - major pollutants: CO, NO_x, SO_2, H_2S, COS, CS_2, mercaptans, CH, particulates and organics,
    - measurement point: level 0 around Generator Section, and
    - measurement magnitude: air composition.
2. Measurement point No. (2): Area around the water cooling section:
    - cause of pollution: exchanger leakage in Gasification Plant sections,
    - major pollutants: volatile components,
    - measurement point: level 0 around water cooling section, and
    - measurement magnitude: air composition (CO, NO_x, SO_2, H_2S, COS, CS_2, mercaptans, CH, particulates, and organics.

3. Measurement point No. (3): Area surrounding Tar Separation Section:
   - cause of pollution: technological design providing direct connection of all vessels with atmosphere by vents,
   - major pollutants: volatile phenols, H_2S and higher hydrocarbons,
   - measurement point: level 0 near tank vents or level 3 on the platform near the vents, and
   - measurement magnitude: air composition (CO, NO_x, SO_2, H_2S, COS, CS_2, mercaptans, CH, particulates, and organics).

PROBLEMS

As already stated, the reported program of research should be completed over a 3-year period. In accordance with this and by gaining insight into all problems connected with the designed works, a Dynamic Time Schedule was made for the realization of the program and enclosed here in table form.

By to-date investigations the following was observed:

Kosovo lignite falls into a group of younger coals and has high contents of moisture (50 percent) and ash (about 30 percent at 105 °C). The coal substance consists of macerals textinite, ulminite, atrinite, and densinite and it is banded by mineral matters the principal representatives of which are clay, marly limestone, and locally pyrite. When exposed to atmospheric precipitations over a longer period, the coal substance decomposes to dust.

Prior to use in the gasification process, Kosovo lignite is dried by the "Fleissner" process down to a moisture content of approximately 24 percent and screened, so that "Lurgi" generators are fed with class--60 + 6 mm. The dried coal--60 + 6 mm contains about 20 percent of ash and some 1.4 percent of total sulfur (at 105 °C).

The content of volatiles in the product amounts about 56 percent, that of carbon 68.5 percent, hydrogen approximately 5 percent, and nitrogen + oxygen about 26 percent, calculated on pure coal substance (moisture and ash free).

In the process of transportation and transfer,substantial amounts of dust are formed due to its high fragmentation propensity. Its Micum test equals 74 percent. Consequently, particles below 0.5 mm are predominant in undersize - 6 mm. Due to above facts, a large quantity of fine dust occurs in our plant prior to generator feed. This dust causes difficulties in the generator during the gasification process. At generator discharge, thick masses of tar and dust are formed, as well as Ca phenolates, decreasing the diameter of raw gas discharge lines.

The produced raw gas contains a high percentage of various solid, liquid, and gaseous pollutants (dust, tar, lower, and higher hydrocarbons, NCN, H_2S, NO, etc.). The realization of the designed program will result in accurate data on the amounts and kinds of pollutants discharged into the air, water, and solid wastes.

Fusibility of dried Kosovo lignite ash occurs at approximately 1290 °C in oxidative atmosphere. Consequently, the slag is discharged from the generators in unmelted form. Chemical composition of the slag is such that it reacts with water and forms a basic medium of about pH = 11. It is particularly interesting that it contains, in addition to various trace elements, 0.4 percent of stroncium oxide and 0.27 percent of manganese oxide.

The tar produced starts to distill at 264 °C, and the fraction yields are as follows:

264 - 300° C	9.0 percent (water free)
300 - 335° C	23.0 percent (water free)
+ 335° C	68.0 percent (water free)

The tar solidification temperature is 48 °C. The rate of pollution in the Tar Separation Section is very high due to discharges from the tanks through vents directly into the atmosphere.

The analyses of clean gas used for separating the hydrogen required for ammonium synthesis indicate that clean gas contains hydrocarbons (C_3H_6,C_3H_8) and nitrogen oxides, so that its use for ammonium production is questionable.

The cause of environmental pollution from Kosovo Coal Gasification Plant in Obilic should, naturally, primarily be looked for in the grade of available raw material which we are forced to process, as well as in the technological processes and facilities designed and selected at the time when little consideration was paid to environmental pollution, i.e., when preventive solutions were not required.

We are sure that the results of our investigations will be of overall usefulness and advantage, and particularly for us in Socialist Autonomous Province Kosovo, since this knowledge will enable us to improve the operation of individual existing facilities and processes, as well as to select more efficient and more adequate procedures in possible future construction of gas production plants leading to efficacious protection of our living environment.

Thanks for your attention!

FATE OF POLLUTANTS IN INDUSTRIAL GASIFIERS

By
Gordon C. Page
Radian Corporation
8500 Shoal Creek Boulevard
Austin, Texas 78758

Abstract

There is currently a growing interest in using low-Btu gas produced from coal as a combustion fuel for industrial boilers, kilns, and furnaces. In light of this, the Environmental Protection Agency has initiated a comprehensive assessment program with Radian Corporation to evaluate the environmental impacts associated with this growing technology.

The purpose of this paper is to present the current data on the fate of pollutants from industrial gasifiers used to produce low-Btu combustion gas from various types of coal. The two gasification systems considered in this paper use atmospheric, fixed-bed, single-stage gasifiers; one produces a hot gas, the other a cooled or quenched low-Btu gas.

Data on the fate of sulfur and nitrogen species, organics, trace elements, and particulate matter are presented. Analyses of these data indicate that: a) 81 to 97% of the coal sulfur can be converted to H_2S and COS in low-Btu gas produced from high volatile bituminous coals and lignite having the lower sulfur conversion, b) the amount of NO_x formed by combusting low-Btu gas should be lower than direct-firing of coal; however, there may be a potential for incomplete combustion of NH_3 and HCN in the low-Btu gas, c) there are small amounts of organics in the gasifier ash and cyclone dust (20 to 380 ppm, respectively); however, quench liquors will contain high concentrations of organics consisting primarily of phenols, d) from trace element analysis of the gasifier ash, cyclone dust, quench water, and by-product tar, the cyclone dust had the highest amounts of Pb, Se, As, and Fl while the by-product tar was highest in Hg, and e) the physical and chemical characteristics of the particulate matter entrained in the low-Btu gas are highly dependent on coal type and gasifier operating parameters.

INTRODUCTION

In recent years the nation's energy picture has changed drastically due to increasingly severe shortages of oil and natural gas. Because of these shortages, there is currently a growing interest in using low-But gas (~150 Btu/scf) produced from coal as a combustion fuel for industrial boilers, furnaces, and kilns. In response to this, the Environmental Protection Agency has contracted Radian Corporation to perform a multimedia environmental and control technology assessment for low/medium-Btu gasification technology.

To date, there are little actual data on the environmental and health effects of the discharge steams from low-Btu gasification systems, along with the technology used to control these streams. In light of this, one of the main objectives of the low-Btu environmental assessment program is to characterize the nature of the waste streams generated by commercial low-Btu gasification plants.

The purpose of this paper is to present current data on the fate of pollutants from industrial gasifiers producing low-Btu gas. The two gasification systems considered in this paper use atmospheric, fixed-bed, single-stage gas producers with one system producing a hot combustion gas and the other a cooled/quenched gas. The coal feedstocks considered for these systems include anthracite, high volatile bituminous, low volatile bituminous, and lignite. The sulfur concentrations of these coals ranged from 0.6 to 3.7 weight percent.

The information given in this paper deals with the fate of sulfur and nitrogen species in low-Btu gasification systems along with the nature and content of organic compounds, trace elements, and particulate matter in the multimedia discharge streams. Conclusions that can be drawn from these data and recommendations for further work are also discussed.

System I

System I for producing low-Btu gas from coal is illustrated in Figure 1. This system contains the following three process modules: a) an atmospheric, fixed-bed, single-stage gasifier, b) a hot cyclone, and c) a combustion process.

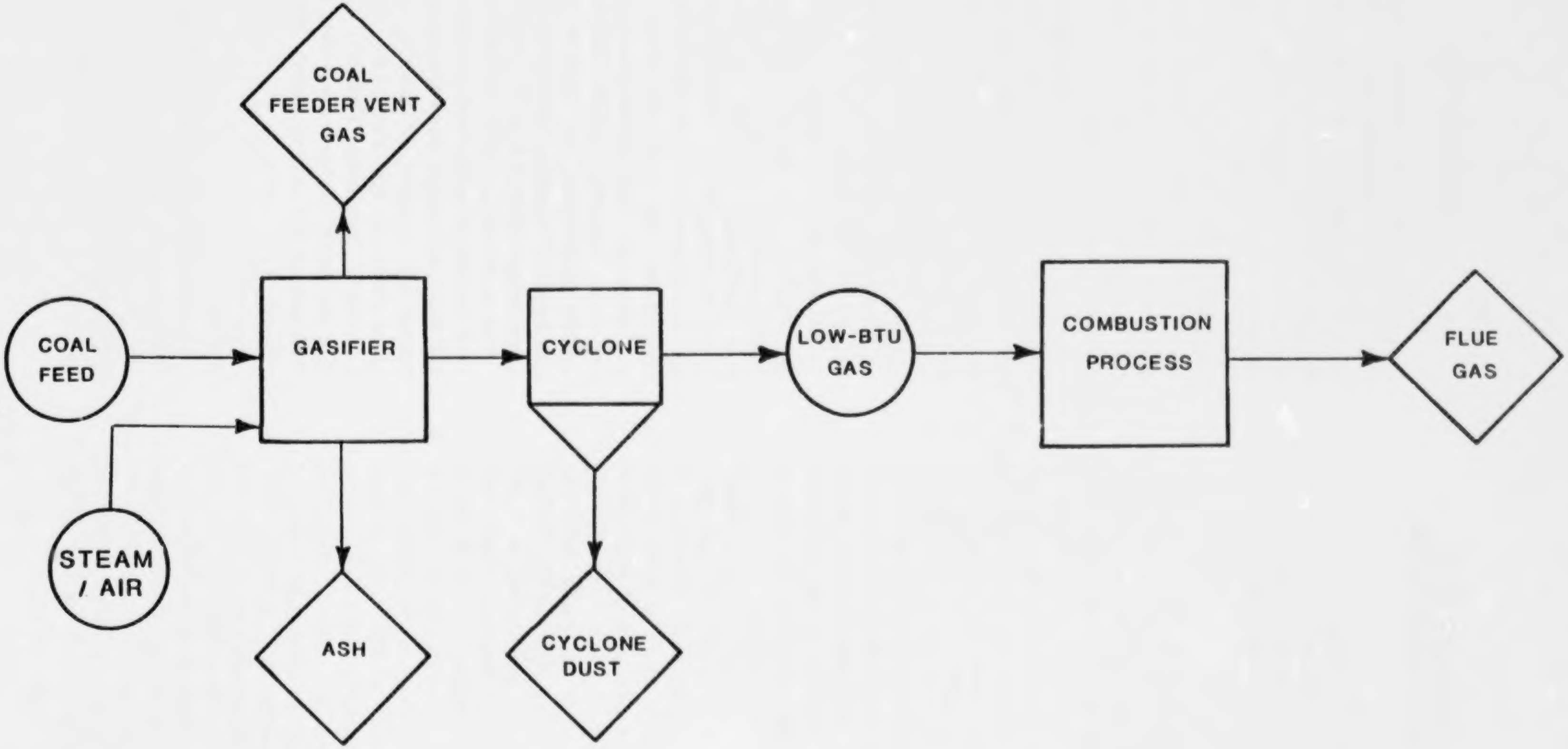

COAL FEED
STEAM / AIR
GASIFIER
COAL FEEDER VENT GAS
ASH
CYCLONE
CYCLONE DUST
LOW-BTU GAS
COMBUSTION PROCESS
FLUE GAS

Figure 1. Low-Btu gas production.

Coal is fed into the gasifier where it is reacted with steam and oxygen to produce a hot (~870°K, 1100°F) low-Btu gas having a higher heating value of approximately 150 Btu/scf. The hot gas then enters the cyclone where entrained particulate matter is removed. The particulate-free gas is then combusted.

The discharge streams from this gasification system include both gaseous emissions and solid wastes. The gaseous emissions are the coal feeder vent and combustion gases. The solid wastes are the gasifier ash and the particulate matter collected by the cyclone (cyclone dust).

System II

Figure 2 illustrates System II for producing low-Btu gas from coal. This gasification system contains the same process modules as System I with three additional modules: a) a gas quench, b) a tar/liquor separator, and c) a tar combustion process. This system also has a water pollution control module, forced evaporation, to control the spent quench liquor.

As in System I, coal is reacted with steam and oxygen to produce a hot, low-Btu gas. The particulate matter in the gas exiting the gasifier is removed by a hot cyclone. The particulate-free gas is then quenched and cooled to remove the tars and oils and sent to the gas combustion process. The tar is separated from the quench liquor in a separator and sent to the tar combustion process. The quench liquor from the separator is then recycled to the gas quenching process. Any liquor build up in the system is sent to a force evaporator where volatile liquids are vaporized and vented to the atmosphere.

The discharge streams from this gasification system include gaseous emissions, liquid effluents and solid wastes. The gaseous emissions are the coal feeder and tar/liquor separator vent gases; and the flue gases from the low-Btu gas and tar combustion processes. The liquid effluent is the spent quench liquor while the gasifier ash and cyclone dust are the solid wastes.

COAL FEEDSTOCKS

The data presented in this paper were obtained during the production of low-Btu gas from six different coal feedstocks. The proximate and ultimate analyses and the higher heating values for these coals are given in Table 1. These feedstocks include anthracite-, bituminous-, and lignite-type coals which are representative of the various types of coals which are or will be used to produce low-Btu gas on a commercial scale.

POLLUTANTS FROM LOW-BTU GAS PRODUCTION

In this section the fate and characteristics of the pollutants from the two gasification systems producing low-Btu gas from various coal feedstocks are discussed. The fate of coal sulfur and the concentrations of specific sulfur species in the low-Btu gas are presented. The fate of coal nitrogen and specific nitrogen containing compounds in the product gas are discussed along with data concerning the combustion of these nitrogen-containing compounds. The nature and content of organics and trace elements in liquid and solid waste streams are presented followed by a discussion of the physical characteristics of the particulate matter entrained in the product gas.

Sulfur Series

The fate of sulfur species during the gasification of high volatile A (HVA) bituminous and lignite coals is given in Table 2. According to these data, approximately 97 percent of the HVA bituminous coal sulfur was converted to H_2S and COS while only 81 percent of the lignite sulfur was converted. This variation is probably due to the chemical characteristics of the lignite ash since alkaline ashes will retain significant amounts of sulfur. This is exemplified by the high sulfur content (14.2%) found in the ash from gasifying lignite. This phenomenom has also been demonstrated in fluidized-bed combustion tests for lignite.[4]

The actual amounts of sulfur species in the process and discharge streams from gasification systems I and II are given in Table 3. There are no data on five of the discharge streams from these systems: a) the coal feeder vent gases, b) the tar/liquor separator vent gases, c) tar combustion gases, d) low-Btu gas combus-

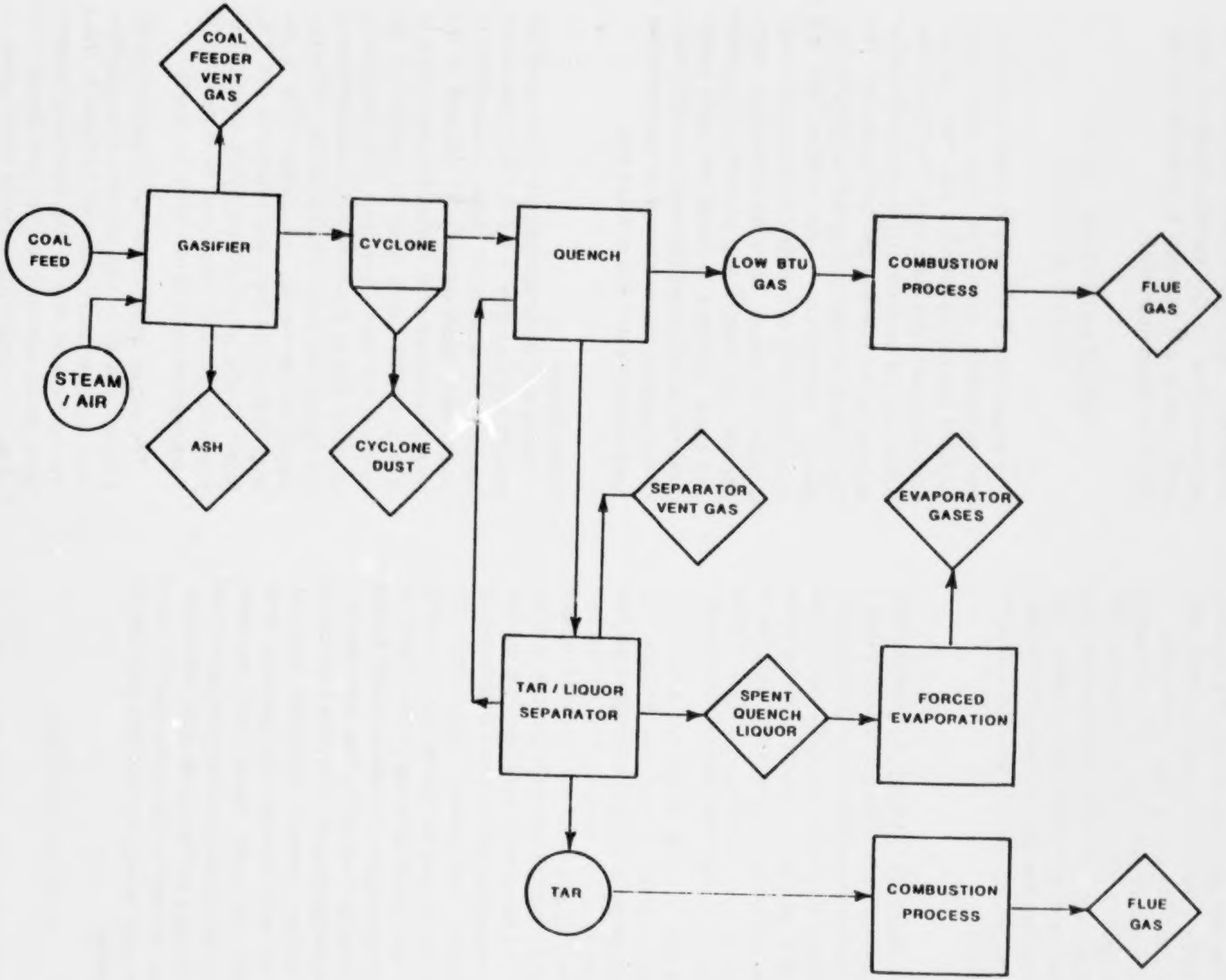

COAL FEED
STEAM / AIR
GASIFIER
COAL FEEDER VENT GAS
ASH
CYCLONE
CYCLONE DUST
QUENCH
LOW BTU GAS
COMBUSTION PROCESS
FLUE GAS
SEPARATOR VENT GAS
TAR / LIQUOR SEPARATOR
SPENT QUENCH LIQUOR
FORCED EVAPORATION
EVAPORATOR GASES
TAR
COMBUSTION PROCESS
FLUE GAS

Figure 2. System II—Low-Btu gas production.

TABLE 1

COAL FEEDSTOCK ANALYSES FOR FIXED-BED, ATMOSPHERIC GASIFICATION SYSTEMS

	Anthracite		High Volatile A Bituminous		High Volatile C Bituminous	Medium Volatile Bituminous	Lignite
Proximate Analysis (wt %)							
Moisture	3.6	5.5	3.5	2.3	7.2	7.1	32.1
Ash	8.0	7.1	4.5	5.0	15.7	5.0	7.6
Volatile Matter	3.6	30.8	29.1	36.4	34.4	21.4	29.0
Fixed Carbon	84.8	56.6	62.9	56.3	42.7	66.5	31.3
Ultimate Analysis (wt %, dry)							
Carbon	86.6	80.0	81.0	—	62.3	85.2	64.8
Hydrogen	2.0	5.1	5.0	—	4.7	4.7	4.5
Nitrogen	}2.3	}6.6	1.5	—	1.0	}4.0	1.5
Oxygen			3.9	—	5.7		17.0
Sulfur	0.8	0.8	0.7	0.6	3.7	0.7	1.0
Ash	8.3	7.5	—	—	—	5.4	11.2
HHV (Btu/lb as received)	11,430	13,405	14,335	13,960	11,315	13,830	7327

Sources: Refs. 1, 2, 3.

TABLE 2

FATE OF COAL SULFUR IN ATMOSPHERIC, FIXED-BED, SINGLE-STAGE, LOW-BTU GASIFICATION SYSTEMS

Coal Sulfur Converted To	Coal Type HVA Bituminous	Lignite
H_2S (wt %)	95.1	78.4
COS (wt %)	2.0	3.1
Tar Sulfur (wt %)	2.1	3.3
Cyclone Dust Sulfur (wt %)	0.7	1.0
Gasifier Ash Sulfur (wt %)	0.1	14.2
	100.0	100.0

TABLE 3

SULFUR SPECIES IN THE PROCESS AND MULTIMEDIA DISCHARGE STREAMS FROM LOW-BTU GASIFICATION SYSTEMS

Coal Type	Gasification System	Coal Sulfur (wt % dry)	Low-Btu Gas Sulfur (ppmv)	Tar/Oil Sulfur (wt %)	Cyclone Dust Sulfur (wt %)	Gasifier Ash Sulfur (wt %)
Anthracite	I	0.8	H_2S = 900	—	—	—
HVA Bituminous	I	0.8	H_2S = 1634 COS = 60	0.5	0.7	0.01
HVA Bituminous	II	0.7	H_2S = 1200	0.5	—	—
HVC Bituminous	II	3.7	H_2S = 11,000	1.6	—	—
Medium Volatile Bituminous	I	0.7	H_2S = 1213 COS = 50	—	—	—
HVA Bituminous	II	0.8	—	520 ppm*	0.67	250 ppm*
Lignite	I	0.91	H_2S = 2877 COS = 133	1.3	2.0	4.1

*SSMS Analysis
Sources: Refs. 1, 2, 3,

tion gases, and e) the vapors from the forced evaporation of the quench liquor.

The data in Table 3 indicate that the amount of COS formed during the gasification of all the coals is approximately 4 volume percent of the total gaseous sulfur species. This amount of COS in the product gas will affect the selection and design of an acid gas removal process to remove H_2S from low-Btu gas. The sulfur content of the tar produced in gasifying lignite was two to three times greater than for gasifying HVA bituminous coals having similar amounts of sulfur. This would indicate that the sulfur emissions from a combustion process using tar produced from lignite would be significantly greater than using tar produced from HVA bituminous coal having the same amount of sulfur. There were also higher concentrations of sulfur in the cyclone dust and ash produced in gasifying lignite compared to gasifying HVA bituminous coals.

Nitrogen Species

In this section the formation of gaseous nitrogen species during coal gasification and the subsequent combustion of these components is discussed. The two gaseous nitrogen species of importance are ammonia and hydrogen cyanide. The date, there are minimal data on the amount of HCN in the product low-Btu gas with no data on the amount of HCN in the following discharge streams: coal feeder and tar/liquor separator vent gases, forced evaporator vapors, and combustion gases from burning the low-Btu gas. However, there are data on the concentration of ammonia in low-Btu gas along with estimates on the fate of ammonia during low-Btu gas combustion.

The current data on the formation of NH_3 and HCN during the gasification of high and medium volatile bituminous coals are given in Table 4. These data indicate that there can be a significant variation in the amount of ammonia formed during the gasification of the same coal feedstock. These variations can probably be attributed to the following operating parameters:

- Amount of steam used to gasify the coal
- Surface moisture content of the coal
- Time-temperature history of the coal particle in the gasifier.

The first two variables affect the hydrogen partial pressure inside the gasifier which is directly proportional to the amount of NH_3

TABLE 4

COAL NITROGEN CONVERTED TO NH_3 AND HCN

	Coal Nitrogen (wt %)	Ammonia Concentration in Low-Btu Gas (ppmv)	Hydrogen Cyanide Concentration in Low-Btu Gas (ppmv)	Molar Conversion of Coal Nitrogen to Ammonia (%)
High Volatile A Bituminous	1.5	109	107	—
High Volatile A Bituminous	1.54	1940		35.0
		622		12.0
		385		5.2
		666		9.0
		486		5.3
		658		7.2
		452		6.8
Medium Volatile Bituminous	1.0	113	129	—

Sources: Refs. 1, 2

formed. The last variable would affect the amount and characteristics of nitrogen intermediates formed in the gasifier.

The data in Table 4 also show the molar conversion of coal nitrogen to ammonia. For all tests except one where the molar conversion was 35.0 percent, the conversions were fairly consistent with the average molar conversion of coal nitrogen to NH_3 being approximately 8 percent.

The amount of HCN in the product low-Btu gas is also significant and deserves special attention when designing low-Btu gas cleaning or combustion processes. Hydrogen cyanide will affect the performance of certain acid gas removal processes that are currently being proposed for cleaning low-Btu gas produced from high sulfur coals. For example, HCN will cause a build up of thiocyanates in the solvent used in a Stretford process.

The fate of nitrogen species during the combustion of low-Btu gas has been investigated with respect to the amount of NH_3 converted to NO_x[2]. These studies indicated that the conversion of coal nitrogen to NO_x in low-Btu gasification systems was approximately 3 to 4 percent. This is much lower when compared to the direct combustion of coal where 10 to 15 percent of the coal nitrogen is emitted as NO_x.

There are, however, two other aspects to be considered in assessing the characteristics of nitrogen species in combustion gases. These are the amounts of NH_3 and HCN not converted to NO_x. The amount of ammonia emitted in the combustion process flue gas can be estimated from Figure 3. For example, if the NH_3 concentration in the low-Btu gas is 500 ppmv, 54 percent will be converted to NO_x while 46 percent will be emitted as NH_3. There are currently no data on the amount of HCN converted to NO_x in a low-Btu gas combustion process. Therefore, the quantity of HCN in the combustion gases is unknown.

Organic Species

The information presented in this section is primarily concerned with the amount and characteristics of the organic compounds in the following process and discharge streams from low-Btu gasification systems:

- Quench liquor
- Cyclone dust
- Gasifier ash
- By-product tar

The first three of these streams represent discharge streams while the byproduct tar is the feed to the tar combustion process.

Total Organics - Grab samples of the quench liquor, cyclone dust, and ash were collected from a gasification plant represented by System II as shown in Figure 2. The feedstock to this plant was a high volatile A bituminous coal. The total amount of organics in these three streams is presented in Table 5. The values for the total amount of organics were determined using the methods specified by the EPA Level 1 Environmental Assessment procedures[3] plus an additional ether extraction for the quench liquor. From the data in Table 5, the spent quench liquor contains a significant quantity of organics (~4000 mg/l). Since this liquor is sent to a forced evaporator, there is a potential for significant vapor emissions. However, there are no data on the emissions from this evaporator.

Organic Characteristics - The characteristics of the organic species in the quench liquor, by-product tar, and cyclone dust are shown in Figure 4. These results were obtained by using the extraction, column chromatography, and infrared (IR) spectra analysis methods specified by the EPA Level 1 Environmental Assessment[5].

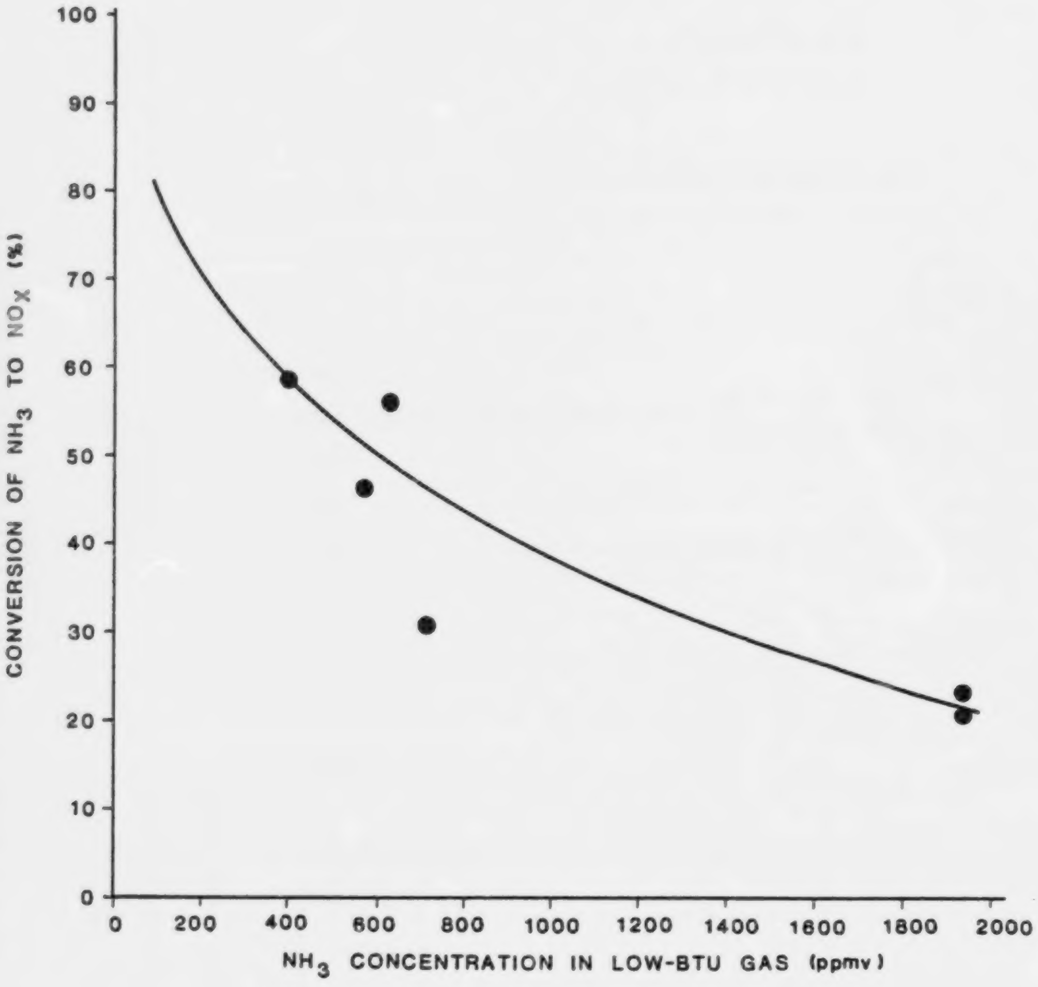
The organic components in the quench liquor consisted primarily of phenols with smaller amounts of acids. The by-product tar contained

TABLE 5

ORGANIC CONCENTRATIONS IN AQUEOUS AND SOLID WASTE DISCHARGE STREAMS FROM LOW-BTU GASIFICATION SYSTEMS

Discharge Stream	Organic Concentration
Spent Quench Liquor	3865 mg/l
Cyclone Dust	381 ppm
Gasifier Ash	18 ppm

Source: Ref. 3.



SOURCE: L-2137

Figure 3. Conversion of ammonia to NO_x in a turbulent-diffusion flame.

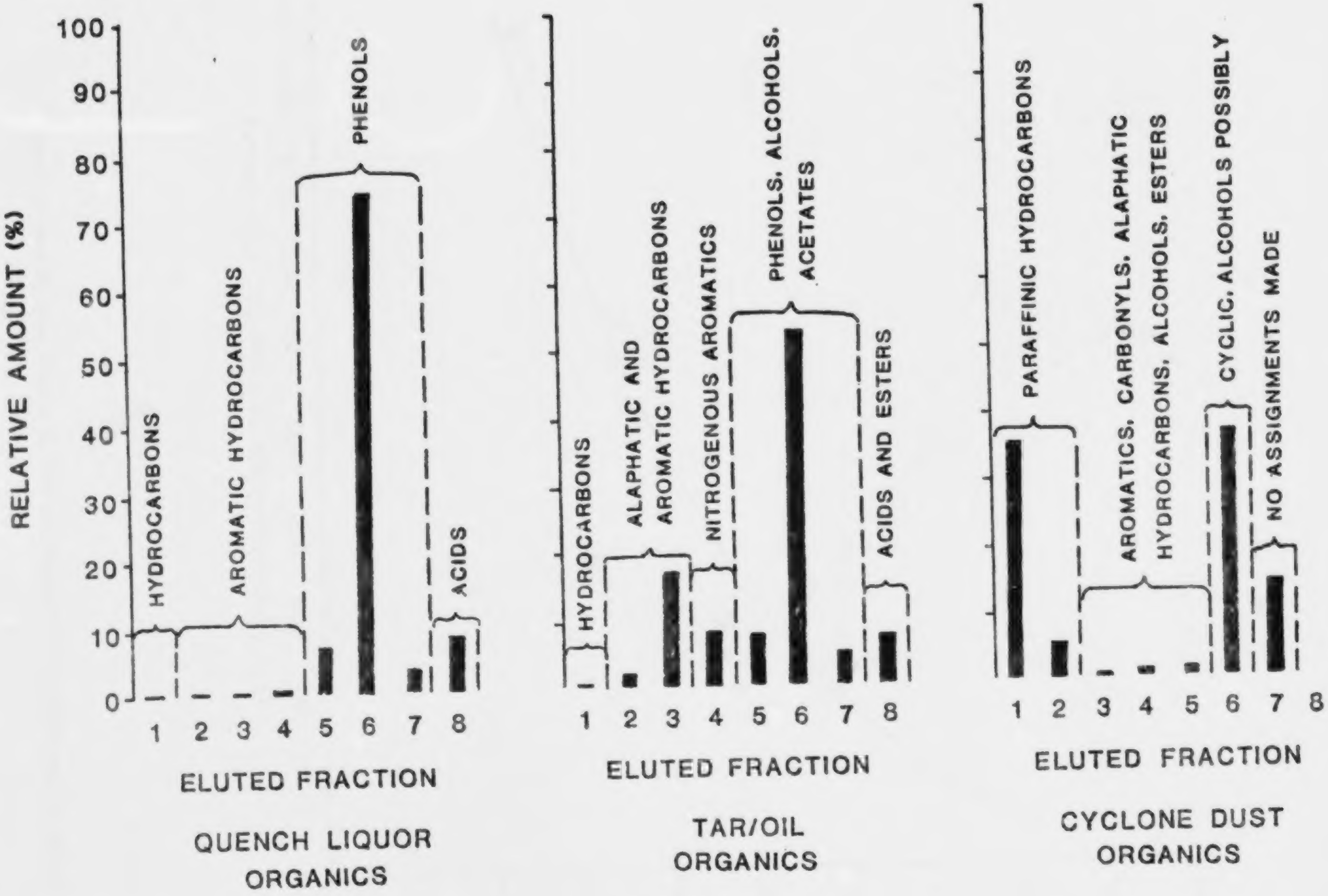


Figure 4. Results of Level 1 organic extraction, column chromatography, and IR analysis (bituminous coal).

a wide range of organic compounds including phenols, alcohols, acetates, acids, esters, etc. The organic constituents extracted from the cyclone dust were primarily paraffinic hydrocarbons and possibly cyclic alcohols. It should be emphasized that using IR spectroscopy to identify the nature of organic species is subject to doubt, especially for complex mixtures. Therefore, caution must be exercised in interpreting the spectra of these mixtures.

Trace Elements

Grab samples of the ash, cyclone dust, quench liquor, and byproduct tar were collected and analyzed for trace elements using Spark Source Mass Spectrometry (SSMS). These samples were taken from a gasification plant similar to System II. The results of these analyses are presented in Tables 6 through 9. A summary of the data in these tables is given in Table 10. From the data in Table 10, the trace element concentrations in the byproduct tar are higher than the quench liquor except for selenium and sulfur.

The six trace elements highlighted in Table 10 indicate certain important aspects of trace element distribution in these samples. The levels of Pb, Hg, As, Fl, and B are higher in the tars compared to the quench liquor while Se levels are essentially the same, Hg levels in the tar are also higher than in the cyclone dust.

In order to identify which trace elements need to be controlled in the spent quench

TABLE 6

TRACE ELEMENTS IN GASIFIER ASH BY SSMS

Element	ppm w/w	Element	ppm w/w	Element	ppm w/w
Uranium	56	Niobium	82	Thorium	86
Zirconium	430	Bismuth	0.4	Yttrium	260
Lead	7	Strontium	MC	Thallium	0.5
Rubidium	120	Rhenium	0.3	Bromine	12
Tungsten	10	Selenium	20	Tantalum	2
Arsenic	4	Hafnium	10	Germanium	4
Lutetium	2	Gallium	66	Ytterbium	12
Zinc	26	Thulium	1	Copper	540
Erbium	8	Nickel	120	Holmium	11
Cobalt	61	Dysprosium	17	Iron	MC
Terbium	4	Manganese	680	Gadolinium	10
Chromium	510	Europium	5	Vanadium	MC
Samarium	28	Titanium	MC	Neodymium	56
Scandium	29	Praseodymium	42	Calcium	MC
Cerium	260	Potassium	MC	Lanthanum	280
Chlorine	230	Barium	MC	Sulfur	250
Cesium	10	Phosphorus	MC	Iodine	0.3
Silicon	MC	Antimony	1	Aluminum	MC
Tin	4	Magnesium	MC	Indium	STD
Sodium	MC	Cadmium	3	Fluorine	≃56
Silver	<0.3	Boron	130	Molybdenum	22
Beryllium	22	Lithium	190		

MC = Major Component

Note - Any element not listed - Concentration < 0.2 ppm by wt

Carbon, hydrogen, nitrogen & oxygen are excluded from these analyses.

Source: Ref. 3.

TABLE 7

TRACE ELEMENTS IN CYCLONE DUST BY SSMS

Element	ppm/wt	Element	ppm/wt
Bismuth	2	Arsenic	27
Lead	60	Germanium	5
Mercury*	0.01	Gallium	130
Terbium	9	Zinc	85
Gadolinium	2	Copper	130
Europium	1	Nickel	30
Samarium	9	Cobalt	16
Neodymium	21	Iron	MC
Praseodymium	5	Manganese	120
Cerium	45	Chromium	90
Lanthanum	45	Vanadium	100
Barium	460	Titanium	MC
Cesium	1	Scandium	12
Iodine	4	Calcium	MC
Antimony	8	Potassium	MC
Tin	2	Chlorine	720
Indium	STD	Sulfur	MC
Cadmium	<2	Phosphorus	MC
Silver	3	Silicon	MC
Molybdenum	14	Aluminum	MC
Mobium	12	Magnesium	MC
Zirconium	80	Sodium	MC
Yttrium	70	Fluorine	≃720
Strontium	340	Boron	70
Rubidium	33	Beryllium	6
Bromine	20	Lithium	27
Selenium	24		

*Flameless atomic absorption

MC = Major Component

Note: Any element not listed - concentration < 0.2 ppm by wt
Carbon, hydrogen, nitrogen and oxygen are excluded from these analyses.

Source: Ref. 3.

TABLE 8

TRACE ELEMENTS IN QUENCH LIQUOR BY SSMS

Element	μg/l	Element	μg/l
Lead	0.04	Gallium	0.006
Mercury	0.007	Zinc	0.07
Neodymum	≤0.01	Copper	0.1
Praseodymium	0.005	Nickel	0.1
Cerium	0.01	Cobalt	≤0.008
Lanthanum	≤0.01	Iron	3
Barium	0.1	Manganese	0.03
Cesium	1	Chromium	0.03
Iodine	0.5	Vanadium	0.004
Antimony	0.1	Titanium	0.05
Tin	0.02	Scandium	≤0.006
Indium	Std	Calcium	MC
Cadmium	≤0.02	Potassium	MC
Molybdenum	0.06	Chlorine	0.3
Xirconium	0.01	Sulfur	MC
Yttrium	0.004	Phosphorus	MC
Strontium	0.2	Silicon	7
Rubidium	0.03	Aluminum	1
Bromine	0.2	Magnesium	2
Selenium	4	Sodium	MC
Arsenic	0.2	Fluorine	≃2
Geranium	≤0.02	Boron	2
Lithium	0.2		

*Flameless atomic absorption

MC = Major Component

Note: Any element not listed - concentration < 0.004 Carbon, Hydrogen, nitrogen and oxygen are excluded from these analyses.

Source: Ref. 3.

TABLE 9

TRACE ELEMENTS IN TAR BY SSMS

Element	ppm	Element	ppm
Lead	10	Copper	3
Mercury*	0.12	Nickel	5
Neodymium	0.6	Cobalt**	5
Praseodymium	0.3	Iron	120
Cerium	0.5	Manganese	0.9
Lanthanum	0.6	Chromium	3
Barium	27.0	Vanacium	0.8
Cesium	0.1	Titanium	29
Iodine	1	Scandium	0.7
Antimony	0.8	Calcium	630
Tin	0.9	Potassium	100
Molybdenum	1	Chlorine	6
Zirconium	0.7	Sulfur	520
Yttrium	≤0.2	Phosphorus	17
Strontium	10	Silicon	170
Rubidium	0.2	Aluminum	25
Bromine	2	Magnesium	23
Selenium	3	Sodium	71
Arsenic	4	Fluorine	≃22
Germanium	1	Boron	19
Gallium	8	Beryllium	0.1
Zinc	7	Lithium	4

*Flameless atomic absorption

**Heterogeneous

MC = Major Component

Note: Any element not listed - concentration < 0.004 ppm Carbon, hydrogen, nitrogen, and oxygen are excluded from these analyses.

Source: Ref. 3.

TABLE 10

TRACE ELEMENTS IN GRAB SAMPLES BY SSMS

	Ash	Cyclone Bottom Dust	Liquor	Tar
Uranium	56	—	—	—
Bismuth	0.4	<2	—	—
Lead	7	60	0.04	10
Mercury	NR	0.01	0.007	0.12
Barium	MC	460	0.1	27
Antimony	1	8	0.1	0.8
Cadmium	3	< 2	⩽0.02	—
Molybdenum	22	14	0.06	1
Selenium	20	24	4	3
Arsenic	4	27	0.2	4
Zinc	26	85	0.07	7
Copper	540	130	0.1	3
Nickel	120	30	0.07	5
Chromium	510	90	0.03	3
Vandium	MC	100	0.004	0.8
Titanium	MC	MC	0.05	29
Chlorine	230	720	0.3	6
Sulfur	250	MC	MC	520
Fluorine	≃56	≃270	≃2	≃22
Boron	130	70	2	19
Beryllium	22	6	—	0.1
Lithium	190	27	0.2	4

Note. All values expresses as ppm except liquor in which values are expressed as μg/ml.
MC = Major Component

liquor, trace element standards for surface, irrigation, and public intake waters are compared to the trace element concentrations found in the quench liquor. These comparisons are given in Table 11. From these data, the most important trace element requiring control is selenium since the concentration of selenium is approximately 400 times greater than the standards set for surface and public intake waters and 80 times greater than for irrigation water standards.

Particulate Matter

The physical characteristics of the particulate matter entrained in the low-Btu gas produced using various coal feedstocks is presented in Table 12. From these data, the physical characteristics of the particulate matter depend upon both the coal feedstock and gasifier operating conditions.

The particulates collected by the cyclone varied with respect to all three physical characteristics analyzed (average particle diameter (dp), ash content, and bulk density). The particulates collected from the gasification system using anthracite coal had the highest values for all three physical characteristics. The system gasifying lignite coal had the lowest average particle diameter while the system used to gasify bituminous coal had the lowest particulate matter ash content and bulk density. From these data, the particulate characteristics for the gasification of bituminous coals varied significantly which in-

TABLE 11

LEVELS OF TRACE ELEMENTS IN LIQUIDS FROM THE QUENCH LIQUOR AND BY-PRODUCT TAR VERSUS WATER QUALITY STANDARDS

Element	Surface Water	Irrigation Water	Public Water Intake	Liquor μg/l	Tar ppm
Antimony	—	—	—	0.1	0.8
Arsenic	0.05	1.0	0.1	0.2	4
Barium	1.0	—	—	0.1	27
Beryllium	—	—	—	—	0.1
Boron	1.0	0.75	1.0	2.0	19
Cadmium	0.01	0.005	0.01	≤0.02	—
Chromium	0.05	5.0	0.05	0.03	3
Fluorine	—	—	—	2	22
Mercury	—	—	0.002	0.007	0.12
Lead	0.05	5.0	0.05	0.04	10
Manganese	0.05	2.0	0.00	0.03	0.9
Molybdenum	—	0.005	—	0.06	1
Nickel	—	0.5	—	0.07	5
Selenium	0.01	0.05	0.01	4	3
Vanadium	—	10.0	—	—	—
Zinc	5.0	5.0	5.0	0.07	7
Copper	1.0	0.2	1.0	0.1	3

TABLE 12

CHARACTERISTICS OF THE PARTICULATE MATTER ENTRAINED IN LOW-BTU GAS

	Collected by the Cyclone			Not Collected by the Cyclone			Suspended in Tar
Coal Type	Average dp (μ)	Ash Content (wt %)	Bulk Density	Average dp (μ)	Ash Content (wt %)	Bulk Density	Average dp (μ)
Bituminous	170	10.2	0.40	—	—	—	2-20
Bituminous	95	15.4	0.53	20*	10.4	0.31	—
Anthracite	200	47.3	0.93	<1*	54.7	—	—
Lignite	70	23.0	—	—	—	—	—

*Agglomerated
Source: Ref. 3.

dicates the dependency of these characteristics on the gasifier operating parameters.

The particulate matter collected after the cyclone consisted of particulates that settled in or escaped from the main product gas line. The particulates in the tar were collected by solution filtration. The particulates not collected by the cyclone were agglomerated. However, this may not be representative of the actual characteristics of the particular matter passing through the cyclone.

These results indicate that the physical nature of the particulate matter carried over in the product low-Btu gas will probably vary from site to site depending on the type of coal feedstock and the operating parameters of the gasifier. Therefore, the design of cyclones and other particulate collecting devices wll be site specific since the design of these devices is highly dependent upon these physical characteristics.

CONCLUSIONS

Data currently available on multimedia discharge streams is not sufficient to make a completely accurate assessment of the health and environmental effects and control technology requirements for producing low-Btu gas from coal. However, judgments on some of these discharge stream characteristics can be made from the data presented in this paper. The following are specific conclusions and recommendations derived from this study.

Sulfur Species

1) The amount of coal sulfur that is converted to gaseous sulfur species (H_2S and COS) is primarily dependent upon the ash characteristics of the coal feedstock. For example, the amount of feedstock sulfur converted to H_2S and COS in gasifying lignite will usually be significantly less than in gasifying high volatile bituminous coals. This is due to the alkalinity of the lignite ash which retains and/or collects sulfur species.
2) The ratio of COS to the total amount of sulfur species in the low-Btu gas was not highly dependent upon coal feedstocks and remained at about 0.04. This may indicate that the mechanisms for H_2S and COS formation during coal gasification are directly related. If this relationship is valid, the amount of COS in this product gas can be estimated for various coals which can be used as a factor in selecting and designing sulfur recovery processes for low-Btu gasification systems.
3) The concentration of sulfur in the by-product tar is dependent upon the nature of the coal feedstock. Sulfur concentrations were found to be two to three times greater in tar produced from lignite than from high volatile bituminous coal. This would affect the amount of sulfur emissions if the tar is to be used as a combustion fuel.

Nitrogen Species

1) The amount of ammonia produced during coal gasification is dependent upon the quantity of steam used, coal feedstock moisture content, and the time-temperature history of a coal particle in the gasifier. Generally, less that 10 mole percent of the coal nitrogen is converted to NH_3 in systems designed to produce low-Btu gas for combustion fuel.
2) The amount of NO_x formed during the combustion of low-Btu gas is a function of the NH_3 concentration in the product gas and the combustion process operating parameters. Past studies have indicated that NO_x formation would be two to three times lower when burning low-Btu gas compared to burning the coal feedstock directly.
3) There may be significant quantities of NH_3 and HCN in the flue gases from low-Btu combustion processes. The current data indicate that up to 50 percent of the NH_3 in the product gas can be emitted in the combustion gases while there is no actual data on the amount of HCN emitted.

Organics

1) The liquor used to quench low-Btu gas will contain significant quantities of

organic compounds consisting primarily of phenols. Forced evaporation of large quantities of spent quench liquor will cause a significant quantity of organics to be emitted into the atmosphere.

2) The ash produced from coal gasification will contain very small quantities of organics (~20 ppm) while the organics in the particulate matter entrained in the product gas will be much higher (~400 ppm).

Trace Elements

1) Concentrations of Pb, Se, As, and Fl were highest in the cyclone dust compared to the ash, quench liquor, and by-product tar while the Hg concentration was highest in the by-product tar.
2) The levels of trace elements in the quench liquor equaled or exceeded the levels listed in the Federal Water Quality Standards for nearly every element. The largest deviation was shown by selenium at 4 ppm (400 times greater than the standard for surface water).

Particulate Matter

1) The particulate matter entrained in the low-Btu gas had different particle size distributions, bulk density, and ash contents. These physical and chemical properties seem to be dependent on coal type and the gasifier operating characteristics. These variations will significantly affect the operation of cyclones and other collection devices used to remove particulate matter from the product gas.

RECOMMMENDATIONS

The characteristics of certain discharge streams should be determined. There are currently no data on the composition of the following streams: coal feeder and tar/liquor separator vent gases, vapors from the forced evaporation of spent quench liquor, and tar combustion gases. There are some data on the flue gases produced during the combustion of low-Btu gas; however, the fate of trace constituents such as HCN in these combustion processes has not been determined. The organic constituents in the spent quench liquor need to be further characterized and leaching tests for the ash and cyclone dust need to be performed.

In conjunction with further characterization of the multimedia waste streams from low-Btu gasification systems, methods to determine the health and environmental effects of these streams need to be developed. These methods will provide the goals for control technology implementation and development along with defining technologies necessary to minimize worker exposure to hazardous fugitive emissions from these processes.

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LIQUEFACTION ENVIRONMENTAL ASSESSMENT

Dwight B. Emerson
Hittman Associates, Inc.
9190 Red Branch Road
Columbia, Maryland 21045

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Abstract

Part of Hittman Associates environmental assessment of coal liquefaction processes has been the development of functionally discrete unit modules, composed of an aggregation of unit process operations. This paper presents an overview of the current liquefaction process technology and applicable control technology based on the unit module approach. Eleven unit modules are developed including: Coal Preparation, Hydrogenation, Pyrolysis/Hydrocarbonization, Hydrotreating, Catalytic Synthesis, Supercritical Gas Extraction, Phase Separation, Fractionation, Acid Gas Removal, Hydrogen/Synthesis Gas Generation, and Auxiliaries/Utilities.

INTRODUCTION

With the entry into an era of declining petroleum reserves, reduced discoveries, escalation of prices, and real or induced shortages, coal liquefaction technology has once more assumed a major role as a potential solution to liquid fuel problems. Currently some twenty-odd processes are in various stages of development by industry and federal agencies.

All liquefaction processes achieve the objective of producing liquids by yielding a material having higher hydrogen content than coal. Hydrogen is present in coal at a level of about 5 percent. In high-Btu gas it is roughly 25 percent. Fuel oils contain 9 to 11 percent hydrogen and gasoline about 14 percent. Whether the required hydrogen increase is obtained by adding hydrogen to the coal components or by stripping the hydrogen-rich components from the coal depends upon the particular process. It also affects the yield of liquid from the process.

Environmental Assessment Definition

In their efforts to assist in the development of an environmental assessment methodology protocol, the EPA IERL-RTP supported contractors have used the term environmental assessment to mean a continuing iterative study aimed at:

(1) determining the comprehensive multimedia environmental loadings and environmental control costs, from the application of the existing and best future definable sets of control/disposal options, to a particular set of sources, processes, or industries; and
(2) comparing the nature of these loadings with existing standards, estimated multimedia environmental goals, and bioassay specifications as a basis for prioritization of problems/control needs and for judgement of environmental effectiveness.

Included in Hittman Associates' liquefaction environmental assessment program are six basic components. They are: (1) Current Process Technology Background, (2) Environmental Data Acquisition, (3) Current Environmental Background, (4) Environmental Objectives Development, (5) Control Technology Assessment, and (6) Environmental Alternatives Analysis. This paper presents an overview of the modular approach used during Hittman's initial efforts at current process technology description and control technology assessment.

UNIT MODULES

Although significant technical differences exist between the liquefaction processes, many individual unit and process operations are common to two or more processes. Further, at the present stage of development, most published process designs are only conceptual, and significant differences between the current design and future commercial plants are certain to arise.

To avoid the redundancy of studying each unit operation in each process, and the hazards associated with conceptual designs, unit operations were grouped within a series of functional modules. Each module was structured to perform a specific function, for example, hydrotreating, to remove S, N and O from liquid hydrocarbons.

Each module is composed of one or more individual unit operations or unit processes. Because of the functional orientation, the streams entering and leaving a module will be essentially the same, even though the individual components of the module may be slightly different for different processes.

Process streams are defined as any stream entering a module and any stream leaving a module having as its destination another module. Waste streams are defined as those streams leaving a module having as destinations either a control system or the environment. Eleven modules were developed to characterize the unit operations contained in coal liquefaction processes.

Coal Preparation Module

Operations which are performed in the coal preparation module include crushing, grinding, pulverizing, screening, drying, slurry preparation, and preheating. In general, crushing, grinding, drying, and screening will be included in the module for all processes. Pulverizing is included as well for several processes, and all of the hydrogenation processes which use a solvent will use slurry preparation and preheating.

Process streams leaving this module are either prepared coal or heated coal/oil slurry. Waste streams include particulates from mechanical operations and stack gas from drying. Processes which slurry and preheat the coal will have an additional stack gas stream as well as potential venting of gases.

Hydrogenation Module

In this module hydrogen is added to the "coal molecule." Portions of the coal which can be converted to soluble compounds dissolve leaving an insoluble carbon residue and mineral matter in suspension.

Variations include catalytic, non-catalytic, and donor solvent systems. Since these operations are usually carried out at high pressure, a pressure reducing operation may be included. The crude liquid/solid leaving the reactor may be cooled using waste heat boilers or heat exchangers.

There are only two process streams leaving the module. These are the crude coal liquid and, in some processes, a gas stream. No waste streams are generated continuously, but occasional venting may occur, and periodic replacement of the catalyst will be necessary.

Pyrolysis/Hydrocarbonization Module

High temperature gases are used to strip volatiles from and/or to chemically add hydrogen to coal in this module. Pyrolysis requires introduction of steam and oxygen to react with the coal while hydrocarbonization uses heated hydrogen.

Vapor leaving the pyrolysis or hydrocarbonization reactor is cooled by quenching with either water or oil. Non-condensibles are used elsewhere in the process. Waste heat recovery may precede the quench. The condensed liquid may contain an aqueous phase as well as particulates, and a separation step may be included in the module.

Process streams leaving the module are the crude quenched liquid, noncondensible gas, and the char. Waste streams may include water used to cool the char and excess quench water.

Hydrotreating Module

The purposes of hydrotreating are to remove sulfur, nitrogen, and oxygen compounds via conversion into hydrogen sulfide, ammonia, and water and to further hydrogenate the crude oil.

Hydrotreating is a high pressure and high temperature process. Heat is supplied by plant fuel gas to preheat the crude and the reaction itself is exothermic. The reactor product is depressurized and cooled. An oil and an aqueous phase are formed. The oil is stripped to remove hydrogen sulfide and ammonia.

Process streams leaving the section are a sour gas stream from depressurization, the sour stripping stream, and the purified oil. Waste streams include stack gas, sour water, intermittent vents, and periodic catalyst disposal or regeneration.

Catalytic Synthesis Module

This module catalytically converts synthesis gas into liquid hydrocarbons or methanol.

Operations are heating and pressurizing the feedstock, catalytic conversion, cooling the raw product, and separating byproduct gases and water from the raw product. A sulfur guard reactor may be used to protect the catalyst.

Process streams are liquid hydrocarbons and hydrocarbon gases. Waste streams are water, spent catalyst, spent sulfur guard absorbent, and stack gas.

Supercritical Gas Extraction Module

This module performs a function similar to the hydrogenation module via a completely different route.

A solvent, above its critical temperature and pressure, is used to extract soluble and fusible components from coal. Operations required are compression and heating of the solvent, separation of the solvent/solute mixture from remaining coal material, reduction of mixture pressure, and finally, separation of the extract and solvent.

Phase Separation Module

Solids, liquids and gases are separated in numerous different unit operations. In coal liquefaction processes, situations arise involving two, three, and four phases. The phase separations are gas/solid, gas/liquid, liquid/solid, liquid/liquid, gas/liquid/solid, and gas/liquid/liquid/solid.

Operations include cycloning, filtering, centrifuging, decanting, settling, and depressurizing.

Depending upon where in the process the module is located, process streams and waste streams may be solids, liquids, and gases. Process streams generally will be oils, carbon containing residues, and fuel gases. In general, waste streams will be water, ash or slag, and tars or other heavy residuals. Phase separation modules may be incorporated as an operation in other modules. Under that circumstance, they are not treated as a separate module.

Fractionation Module

The fractionation module separates crude feedstock into product and byproduct components.

Primary operations used may be distillation, vacuum flashing, and stripping. In addition, heat must be supplied, depressurization may be necessary, and cooling is required.

Process streams are: product and byproduct to further processing or storage, recycle process solvent, fuel gases, and solvents. Waste streams may include water and gases, and in rare instances liquid hydrocarbons and solid or semisolid residues.

Acid Gas Removal Module

This module separates hydrogen sulfide from hydrocarbon gas streams. In some instances, carbon dioxide may be separated also.

Operations in the primary section consist of one or more gas/liquid or gas/solid contacts, appropriate temperature and pressure adjustment, and demisting, when necessary. Supporting operations are absorbent regeneration and make up.

Product gas, free of acidic constituents is the main process stream in this module. The primary waste stream is regenerator off gas, hydrogen sulfide, carbon dioxide, or both. Depending upon the system used, spent solid absorbent or solution will also be a waste stream.

Hydrogen/Synthesis Gas Generation Module

The purpose of this module is to produce a reducing gas composed of hydrogen and carbon monoxide. In the case of Fischer-Tropsch and methanol synthesis, the gas is used in catalytic synthesis to produce liquid hydrocarbons. In the other liquefaction processes, the gas is used for either hydrogenation and/or hydrotreating.

Coal gasification, particulate removal, CO-shift, and gas cleanup are the major operations in this module. In addition, there are quenching, cooling, and drying operations. Waste heat recovery is included.

The only process stream leaving the module is the synthesis gas. Because of the numerous operations included in this module, waste streams predominate. Ash, slag, or char will be discharged from the gasifier. Water streams originate in the quench and cooling operations. Particulates are removed from the gas and tars, oils, and other organics are present. A carbon dioxide/hydrogen sulfide stream exits the gas cleanup operation. Spent catalyst will be periodically removed.

Process operations involved in hydrogen generation are the same as those in synthesis gas generation except in two respects: carbon residue or char, supplemental with coal, is used instead of coal alone; and the CO-shift reaction is controlled to produce a much higher hydrogen content. All equipment, operations, process streams, and waste streams are the same as in synthesis gas generation.

Auxiliaries and Utilities Modules

These include the oxygen generation module, where nitrogen is the only waste stream; the make up water module in which waste streams include sludges, brines, and spent regenerant solutions; the cooling water module where waste streams are cooling tower blowdown, evaporation and drift; the stream power generation module where waste streams include stack gas, boiler blowdown and ash; the the product storage module in which the waste streams are intermittent and fugitive losses of vapors, liquids, and particulate during loading and storage periods.

Unit Modules Summary

Table 1 presents a summary of the modules and module components contained in nineteen coal liquefaction processes. Some modules are present in all liquefaction processes. Other modules are specific for particular liquefaction processes, such as catalytic synthesis and supercritical gas extraction.

CONTROL TECHNOLOGIES

Liquefaction processes produce a range of airborne, waterborne, solid, and transient wastes. The data acquisition phases of our environmental assessment program are being structured to provide a more quantified picture of liquefaction related pollutant constituents than that presently available. The modular approach will provide the framework upon which pollutant control technologies can be comparatively assessed.

Air Emissions

The predicted sources and characteristics of air emissions within each process module are specified in Table 2. Flue gas emissions include carbon monoxide, nitric oxides, sulfides, ammonia, and unburned hydrocarbons. The preparation of the coal for further treating can produce particulates and possibly hydrocarbon vapors. Catalyst removal and replacement may be a source of particulates, ammonia, and hydrogen sulfide. In fractionation, uncondensed gases such as H_2S and CO_2 may be emitted. Cooling tower drift and blowdown contains biocides, anti-corrosive agents, and other solids found in the circulating cooling water. Combustion of fuels may produce air emissions such as NO_x, SO_x, hydrocarbons, particulate, and fly ash, depending upon the fuel type used. Hydrocarbons, sulfides, sulfur dioxides, ammonia, and particulates all may be found in the vapors emitted from flash drums used in the phase separation module. From acid gas removal, CO_2 gases are emitted. These gases may include some CO, hydrocarbons and sulfides.

There is a variety of equipment available to control different types of emissions. Table 3 indicates some of the more common technologies. Control of air emissions may result in increased water pollution or solid waste. Particulates containing hydrocarbons, organic and inorganic sulfur compounds, heavy metals, cyanides, etc., must be disposed of. Scrubber wastes include sludges and water containing similar contaminants.

Water Emissions

Almost all modules reject a wastewater stream. The volume and characteristics of water from each module is process specific, but similarities exist among constituents of wastewater from a particular module for all processes utilizing the module. Water requirements for coal liquefaction processes vary

TABLE 1

MODULE COMPONENTS CONTAINED IN MAJOR LIQUEFACTION PROCESSES

LIQUEFACTION PROCESS / MODULE/ MODULE COMPONENT	SRC I	SRC II	H-COAL	EXXON	SYNTHOIL	COED	CSF	COSTEAM	CLEAN COKE	FISCHER-TROPSCH	GARRETT	COALCON	METHANOL	TOSCOAL	ADL	GAS EXTRACTION	BERGIUS	SOLID PHASE HYDROGENATION	LIQUI-COAL
1. COAL PREPARATION	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
A. Crushing	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
B. Drying	+	+	+	+	+	+	+	o	+	+	+	+	+	+	+	+	+	+	+
C. Pulverizing	+	+	+	+	+	o	+	+	+	+	o	+	+	o	+	+	+	+	+
D. Slurry Preparation	+	+	+	+	+	o	+	+	+	o	o	o	o	o	+	+	+	o	+
E. Preheating	+	+	+	+	+	o	+	+	+	o	o	+	+	o	+	+	+	o	+
2. HYDROGENATION	●	●	●	●	●	X	●	●	●	X	X	X	X	X	●	X	●	●	●
A. Catalytic	o	o	+	o	+	o	o	o	o	o	o	o	o	o	o	o	+	o	o
B. Non-catalytic	+	+	o	+	o	o	+	+	+	o	o	o	o	o	+	o	o	+	+
3. PYROLYSIS	X	X	X	X	X	●	X	X	●	X	●	●	X	●	X	X	X	X	X
A. Direct	o	o	o	o	o	+	o	o	o	o	+	o	o	+	o	o	o	o	o
B. Hydrocarbonization	o	o	o	o	o	o	o	o	+	o	o	+	o	o	o	o	o	o	o
C. Cooling	o	o	o	o	o	+	o	o	+	o	+	+	o	o	o	o	o	o	o
D. Quenching	o	o	o	o	o	+	o	o	+	o	+	+	o	o	o	o	o	o	o
4. HYDROGEN/SYNTHESIS GAS-GENERATION	●	●	●	●	●	●	●	●	●	●	●	●	●	X	●	X	●	●	●
A. Coal Gasification	+	+	+	+	+	o	+	+	o	+	o	Y	+	o	+	o	+	+	+
B. Char Gasification	+	+	o	o	o	+	o	o	+	o	+	+	o	o	o	o	o	o	o
C. Particulate Removal/ Quenching	+	+	+	+	+	+	+	+	+	+	+	+	+	o	+	o	+	+	+
D. Shifting	+	+	+	+	+	+	+	Y	+	+	+	+	+	o	+	o	+	+	+
5. CATALYTIC SYNTHESIS	X	X	X	X	X	X	X	X	X	●	X	X	●	X	X	X	X	X	X
A. Trace Sulfur Removal	o	o	o	o	o	o	o	o	o	+	o	o	+	o	o	o	o	o	o
B. Synthesis Reaction	o	o	o	o	o	o	o	o	o	+	o	o	+	o	o	o	o	o	o
C. Cooling	o	o	o	o	o	o	o	o	o	+	o	o	+	o	o	o	o	o	o
6. PHASE SEPARATIONS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
A. Vapor & Gas Separation	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o
B. Solids Removal	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
7. HYDROTREATING	X	X	X	●	X	●	●	X	X	X	●	X	X	X	●	X	X	X	●
A. Preheating	o	o	o	+	o	+	+	o	o	o	+	o	o	o	+	o	o	o	+
B. Catalytic Reaction	o	o	o	+	o	+	+	o	o	o	+	o	o	o	+	o	o	o	+
C. Cooling	o	o	o	+	o	+	+	o	o	o	+	o	o	o	+	o	o	o	+
8. FRACTIONATION	●	●	X	●	X	●	●	X	●	●	X	●	●	X	●	●	●	X	●
A. Product Separation	+	+	o	+	o	+	+	o	+	+	o	+	+	o	+	+	+	o	+
B. Condensation	+	+	o	+	o	+	+	o	+	+	o	+	+	o	+	+	+	o	+
9. ACID GAS REMOVAL	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
A. Absorption	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
B. Regeneration	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
10. SUPERCRITICAL GAS EXTRACTION	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	●	X	X	X
A. Extraction	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	+	o	o	o
B. Quenching	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	+	o	o	o

KEY:

● - Modules Required; X - Modules Not Required; + - Module Components Required; o - Module Components Not Required
Y - Optional Module Components

TABLE 1 (Continued)

LIQUEFACTION PROCESS

LIQUEFACTION PROCESS / MODULE/ MODULE COMPONENT	SRC I	SRC II	H-COAL	EXXON	SYNTHOIL	COED	CSF	COSTEAM	CLEAN COKE	FISCHER-TROPSCH	GARRETT	COALCON	METHANOL	TOSCOAL	ADL	GAS EXTRACTION	BERGIUS	SOLID PHASE HYDROGENATION	LIQUI-COAL
11. AUXILIARY SYSTEMS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
A. Oxygen Generation	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o	+	+	+
B. Makeup & Cooling Water Treatment	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
C. Steam & Power Generation	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
D. Product & Byproduct Storage	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

TABLE 2

SOURCES AND CHARACTERISTICS OF AIR EMISSION

Module	Source	Emission Characteristic
Coal Preparation	Grinding, Pulverizing, and Drying	Particulate, Hydrocarbon vapors
Hydrogenation	Preheater Flue Gas	CO, NO_x, H_2S, NH_3, hydrocarbons
Pyrolysis and Hydrocarbonization	Preheater Flue Gas	CO, NO_x, H_2S, NH_3, hydrocarbons
Hydrotreating	Preheater Flue Gas Catalyst Removal and Replacement	CO, NO_x, H_2S, NH_3, hydrocarbons particulates, NH_3, H_2S
Catalytic Synthesis	Heater Flue Gas	CO, NO_x, N_2S, NH_3, hydrocarbons
Extraction	None	None
Phase Separation	Flash Drum Vapors	Hydrocarbons, sulfides, Sulfur dioxide, Ammonia, particulate
Fractionation	Uncondensed Gases From Condenser	H_2S, CO_2
Gas Cleaning Module	CO_2 Gas Stream	CO_2, H_2S, CO, Hydrocarbons, Sulfides
Synthesis Gas/Hydrogen Generation	Acid Gas CO_2 Stream Driers Flue Gas	CO_2, CO, Hydrocarbons, Sulfides, CO, NO_x, H_2S, NH_3, hydrocarbons
Auxiliary Systems and Utilities	Cooling Tower Drift Boiler Combustion Gases	Biocides, Anticorrosive, Agents, Solids, NO_x, SO_x, Hydrocarbons, Fly ash

TABLE 3

COMMON CONTROL TECHNOLOGIES

Particulate Controls

Dry inertial separators
  cyclones
  multiclones
  baffle chambers
  settling chambers
  impingement separators
  gravity settling chambers
Electrostatic precipitators
Bag (Fabric Filters) Houses
Wet Scrubbers

NO_x Control

Reduction in excess air
  and temperature

SO_2 Controls

Wet Limestone Scrubbing
Limestone Injection

Sulfur Recovery

Claus Plants
Stretford Plants

Gaseous Pollutant Control

Flares
Absorbtion

Evaporation Controls (Mainly Hydrocarbons)

Storage tank modifications
Inspections and maintenance
Vapor collection and recovery equipment

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and wastewater may be treated and reused. In such cases, less of the water utilized will leave the plant as effluent. The type of control and/or treatment required depends on the physical, chemical, and biological properties of the waste stream. All waste streams do not have the same characteristics thus the control technology applicable to waste streams from certain modules will be more extensive than from others. Wastewater streams from some modules may be combined prior to treatment or pretreated separately and then combined for further treatment and discharge.

The sources and characteristics of wastewater streams are shown in Table 4. Coal storage piles have large surface areas and problems may arise as a result of stormwater runoff. Water may react with coal and minerals to form acids or to extract organics, sulfur, and soluble inorganics. Suspended matter are commonly carried by runoff water.

In the pyrolysis and hydrocarbonization module, a significant amount of foul water is generated by the quench operation. Such water contains phenols, tar, light oil, ammonia, sulfides, chlorides, phenolics, and any other products of coal pyrolysis. Vapors separated from pressure let down systems are condensed and such condensates form waste streams also containing phenols, ammonia, light hydrocarbons, and dissolved salts, however the concentration of dissolved salts is lower than that of quench water. Water from the overhead condenser of the hydrotreater has ammonia and sulfides as the primary contaminants but phenols also may be present. Condensate water from fractionation contains sulfides, ammonia, oil, phenols, and dissolved solids. Cooling tower and boiler blowdown may contain high levels of dissolved solids.

Trace elements may appear in both the product and waste streams. Most of the heavy metals will remain in the ash but some of the trace elements will volatilize and may build up in the quench water. Others may be further carried over with acid gases and then appear with purge streams from the acid gas removal module. Of particular interest is the possibility of mercury, selenium, arsenic, molybdenum, lead, cadmium, beryllium, and fluorine in wastewater streams.

The complexity of the wastewater streams from coal liquefaction indicates a need for the utilization of a broad control technology which includes the various treatment processes shown in Table 5. The best practical control technology currently available (BPCTCA) will be a combination of some of these processes. Again, some waste streams will be treated through only part of the whole treatment system depending on the origin of the stream and its characteristics.

Wastewater from the coal preparation module is sent to a separate retention pond to permit the settling of suspended solids. Coagulants may be added for better removal efficiency. Acidity can be controlled by adding limestone. A low biological activity in the retention pond will control any organics that may be present. Higher concentrations of pollutants can be avoided by good housekeeping and by use of silos for storage of small quantities of coal on a day-to-day basis and by covering the coal storage piles with a coating of polymer or asphalt.

TABLE 4

SOURCES AND CHARACTERISTICS OF WASTEWATER STREAMS

Module	Source Description	Wastewater Stream	Constituents
Coal Preparation	Coal storage piles, crushing and grinding operations	Storm water runoff	Suspended particles, dissolved solids
Hydrogenation	Cooling and quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Pyrolysis and Hydrocarbonization	Cooling and quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Hydrotreating	Condensing overhead vapors	Condensate	Phenols, ammonia, sulfi[illegible]
Synthesis Gas Generation	Cooling and quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
	Shifting Operation	Condensed unreacted water	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Catalytic Synthesis	Condensing overhead vapors	Condensate	Phenols, ammonia, sulfides
Phase Separation	Two or three stage pressure reduction	Condensate from overhead condenser	Oils, light hydrocarbons, phenols, ammonia, dissolved sulfides
Fractionation	Cooling overhead vapors	Condensate	Light hydrocarbons, dissolved salts
Gas Cleaning	Absorption and regeneration operations	Purge Flows	Dissolved sulfides in gas removal solvent
Hydrogen Generation	Cooling and quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides, and chlorides
	Shifting Operation	Condensed unreacted water	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Supercritical Gas Extraction	Char quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Auxiliary Systems and Utilities	Cooling towers and boiler	Blowdown	Dissolved solids
	Plant yard area	Storm water runoff	Suspended particles, dissolved solids, traces of phenols, oils and tars

TABLE 5

WASTEWATER TREATMENT PROCESSES

Physical	Chemical	Biological
Sedimentation	Neutralization	Activated Sludge
Flotation	pH Adjustment	Trickling Filter
Oil Separation	Coagulation	Aerated Lagoons
Stripping	Precipitation	Waste Stabilization Ponds
Solvent Extraction	Oxidation	
Adsorption	Ion Exchange	
Combustion		
Filtration		

For oily waste streams containing high amounts of phenols and ammonia, recovery is generally desired. Ammonia is recovered by stripping. After the oil is separated, phenols are recovered by solvent extraction. A probable sequence of processing steps and control process(es) to clean up sour water is as follows:

Removal of H_2S, NH_3, CO_2, light gases
- Stripper

Initial oil and solids removal
- API separators
- Baffle plate separators

Further oil and solids removal
- Clarifiers
- Dissolved air flotation
- Filters

Organic waste removal
- Activated sludge
- Aerated lagoons
- Oxidation ponds
- Trickling filters
- Activated carbon
- Combination

Solid Wastes

Of the many waste streams rejected from various coal liquefaction modules, five basic types of solids waste can be identified. These are particulate coal, ash and slag residues, char, spent catalyst and spent absorbents. Treatment sludges are considered as solid waste generated by control technologies and are discussed below. Particulate coal is generated in the coal preparation module of each liquefaction process. Unreacted coal particles are present in the existing waste streams of other modules as well. Ash consists primarily of metallic oxides, compounds of silicon, aluminum, calcium, iron, magnesium, titanium, sodium, potasium and nickel being the major constituents. In addition, a variety of trace elements are present. Char, although utilized as fuel and to synthesize other process reactants, exits certain modules as waste in minute quantities. Spent catalyst is periodically discharged from modules utilizing them, as is spent absorbent from modules which use absorbents to protect catalysts from acid gases. The solid wastes exiting each module are summarized in Table 6.

Several modules have similar solid waste streams exiting. Spent catalyst and/or spent absorbent are the only solids exiting the hydrogenation, hydrotreating, catalytic synthesis, and gas cleaning modules. Both of these wastes are discharged intermittently. Some catalysts will need changing only every two to three years. The synthesis gas generation, phase separation, fractionation, and hydrogen generation modules will continuously reject ash residue with small amounts of coal and char particles. These streams are the major source of solid waste generated during coal liquefaction process.

In addition, control technologies will generate solid waste streams, including limestone sludges from sulfur dioxide removal systems and water treatment sludges. Calcium sulfite and calcium sulfate are the primary components of limestone sludges. The wastewater sludges will consist primarily of coal tars, sand, coal fines, and water treatment byproducts.

Coal dust particles are generated in the coal processing module. Bag house filters are generally considered the best method of controlling particulate emissions during processing operatons such as grinding and crushing. However, for transferring coal within the preparation module, other vacuum cleaning systems may be preferred. All remaining solid waste streams may be collected without specialized equipment.

Landfilling is the primary technique utilized in solid waste disposal. Ideally, landfill sites will

TABLE 6

MODULAR SOLID WASTE DISCHARGES

Module	Solid Waste					Remarks
	Particulate coal	Spent catalyst	Ash/slag Mineral Matter	Char	Spent (sulfur guard) Absorbent (Zinc sulfide)	
Coal Preparation	+	0	0	0	0	
Hydrogenation	0	+	0	0	0	Spent catalyst not continuously generated
Pyrolysis/Hydrocarbonization	+	0	+	+	0	
Hydrotreating	0	+	0	0	0	Spent catalyst particles in gas or liquid stream
Synthesis Gas Generation	+	+	+	+	0	Spent catalyst not continuously generated
Catalytic Synthesis	0	+	0	0	+	
Extraction (Supercritical Gas Extraction)	0	0	+	0	0	
Phase Separations	+	0	+	+	0	Small amounts of unreacted char/oil may be present
Fractionation	+	0	+	+	0	Solids from donor solvent processes only
Gas Cleaning (Acid gas removal)	0	0	0	0	+	Some systems use sulfur guard absorbents
Hydrogen Generation	+	+	+	+	0	
Auxiliary Systems Utilities	+	0	+	+	0	Particulate product losses during handling, ash and particulates from coal/char burning boilers

+ denotes waste stream is generated in module
0 denotes waste stream is not generated in module

naturally prevent horizontal or vertical migration of solid waste constituent materials to ground or surface waters. Impervious liners may be necessary to assure this. Periodic sampling and analysis of potential leachates is an additional preventive measure.

Utilization of solid wastes to produce useful byproducts is also being considered, with primary emphasis on utilizing ash as a constituent of construction materials, such as asphalt and concrete blocks. Ash has also been used successfully, in the revegetation of mined-out areas. Scrubber sludges, elemental sulfur, phenols, naphtha, and ammonia are other byproducts which could be used beneficially.

Transient Pollutants

Waste streams produced during normal process operation are expected and provisions are made for their disposition on a continuous basis. Consideration must also be given to waste streams generated as a result of intermittent occurrences. These releases may be unplanned or accidental, caused by leaks, spills, upsets, startups, shutdowns, power failure, process equipment failures, slugging, surging, and overloading. They may also be caused by or occur during maintenance operations. Such releases have been termed transient pollutants. Because of their nature they are difficult to sample, analyze, and classify. However, if some thought has been given to these events, it is more likely that the impact of fugitive emissions can be minimized when they do occur. In many cases the best disposition of the waste stream is to return it to the process.

Spills and leaks will occur and provisions for cleanup and containment should be made. Pumps and valves are known sources of leaks. Solids handling equipment can cause problems. Belt conveyors or bucket elevators can break or jam causing spills or fires. In such cases, it may be necessary to dump materials in order to make repairs for resumption of normal operations. Vacuum cleanup trucks could be used to reclaim the spilled solids for reuse. Water flushing can be provided to wash residual solids and to flush oil spills to an "oily water" sewer system for recovery.

During startup, shutdown, or a plant upset, off specification products may be made. Rather than dispose of these materials through the waste treatment facilities, it will probably be much more desirable to store them and rework them into the proper specifications. This procedure, however, will require adequate storage. Enclosed storage will be needed for many of the liquids removed at shutdown. Vapors and particularly odors may be released. Water layers from separations will contain various sulfur, nitrogen, and oxygen compounds that should not be allowed to escape to the atmosphere. These liquids can be stored until a subsequent startup and used for recharge or they can be worked off through the wastewater treating systems.

Before maintenance is performed, the equipment or system will have to be purged to remove toxic and combustible gases. Purge gases should be sent to an incinerator or furnace. This will also be true for shutdowns. Certain catalysts or carbonaceous materials may be pyrophoric at high temperatures. Inert gas purge and cooling will be required to prevent fire.

In the case of plugging, it may be necessary to flush the system with a light oil or with water. Provision must be made to collect and store the cleaning stream until it can be either recycled or treated for disposal. Slugs of liquids may be sent to the flare because of upsets or surges. Serious fires or explosions could be caused if separators are not sized to prevent entrainment.

In general, inspection, monitoring, and maintenance programs are an essential part of controlling transient pollutants.

SUMMARY

A generally applicable modular approach to dividing coal liquefaction processes into groupings of unit operations based on function is proposed. The approach promises to be an effective way of comparatively assessing the waste streams from the wide variety of liquefaction processes. The advantages over alternative, individual process approaches are the ability to comparatively evaluate waste streams from dissimilar unit operations on the basis of module function and to allow for process designs changes as they evolve from conceptual pilot scale to full commercial size.

ACKNOWLEDGMENTS

The paper presented summarizes some of the initial efforts on a comprehensive study entitled Environmental Assessment of Effluents from Coal Liquefaction. The study is supported by the Environmental Protection Agency under Contract No. 68-02-2162.

A PROGRAM FOR PARAMETRIC EVALUATION OF POLLUTANTS FROM A LABORATORY GASIFIER

John G. Cleland, Project Leader
Research Triangle Institute
P.O. Box 12194
Research Triangle Park,
North Carolina 27709

Abstract

Pollutants from gasification processes are being evaluated utilizing a small semibatch reactor. Emphasis is placed on analyzing the production of trace contaminants, especially those presenting potentially pronounced toxic or carcinogenic hazards. Research is progressing in three phases: (1) Chemical screening analyses of the scope of pollutants produced; (2) Evaluation of controlling reactor parameters to reduce specific compounds; and (3) Reactor kinetics studies of first-priority pollutants. Design and construction of the reactor facility and initial baseline tests have been completed.

INTRODUCTION

Work was begun this year at the Research Triangle Institute to investigate some particular pollution problems associated with coal conversion. The research is funded by the Environmental Protection Agency/RTP. The program has recently moved into data accumulation, and the following discussion describes, for the most part, preparation that has been made for the experimental and theoretical research to follow.

With the program still in the early stages, research goals, as determined in coordination with EPA, are being continually defined. Major priorities of this work are, however, clear at present. Emphasis will be placed upon the assessment and analysis of trace pollutants possibly associated with coal conversion processes which have received little attention in the past. This includes particularly investigation of many organic compounds which are associated with carcinogenic or highly toxic properties. Other compounds presenting potential hazards to human health, such as some of the trace elements, will also be included.

When full-scale synthetic fuels plants (e.g., 20,000 tpd of coal) are considered, even trace constituents may be present in significant amounts. Such plants are capable of producing daily (1) more than 15 railroad tank cars of tars and heavy liquids; (2) byproduct waters directly downstream from the reactor containing as much as 340,000 pounds of ammonia, 6,000 pounds of thiocyanates, and 800,000 pounds of phenol; and (3) hazardous contaminants in raw gases, liquids, or solids from the reactor that can possibly find their way into the environment or the synthetic fuel product.

The RTI research is primarily concerned with the nucleus of any coal conversion plant, the reactor, which receives and evolves most of the process streams of environmental interest. While there are certainly other pollution problems in the gas beneficiation and cleanup modules of a plant, the reactor is the major source of compounds going to both product gases and effluent streams.

As indicated in Figure 1, we are also concerneded with the ash, char, particulates, tars, and liquids in reactor outputs. These, along with reactor inputs and product gas, constitute the major mass flows at the front end of any coal conversion system. Research in this area complements (1) other efforts being directed toward environmental control for coal conversion in the Research Triangle area (discussed in other papers at this Symposium) and (2) the intensive on-site sampling and analysis, control options evaluations, and other environmental assessment and control technology development being carried out by prime contractors for EPA; see Figure 2. RTI findings will be compared with EPA analyses being done on a much larger scale, e.g., in joint programs with ERDA or at the Kosovo, Yugoslavia Lurgi gasification plant.

The research at RTI was prompted by several needs and interests of the Environmental Protection Agency:

1. There has been increased emphasis on investigation of toxic constituents in the environment which, in many cases, may be present in relatively low concentrations. This emphasis has been fostered by more extensive and successful cancer research and other related health and medical studies. The

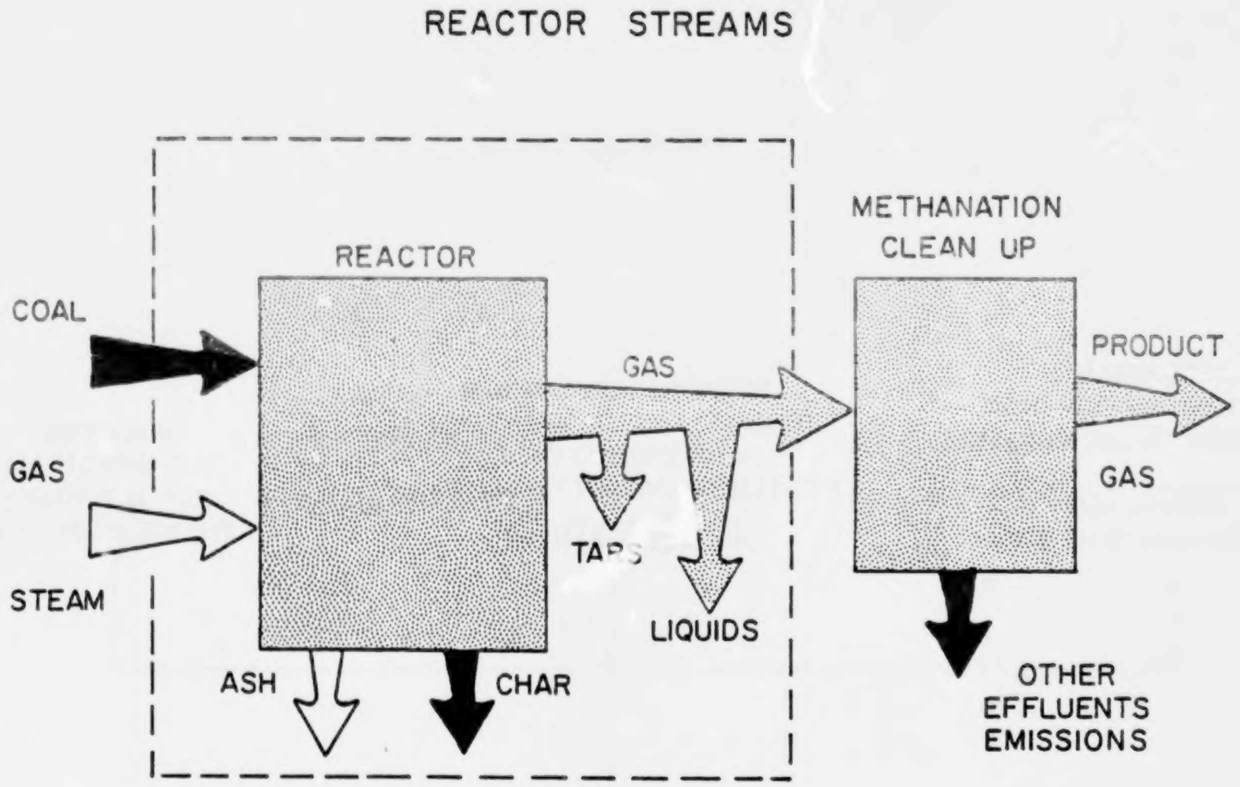
REACTOR STREAMS
REACTOR
COAL
GAS
STEAM
ASH
CHAR
GAS
TARS
LIQUIDS
METHANATION
CLEAN UP
PRODUCT
GAS
OTHER
EFFLUENTS
EMISSIONS

Figure 1. Reactor streams.

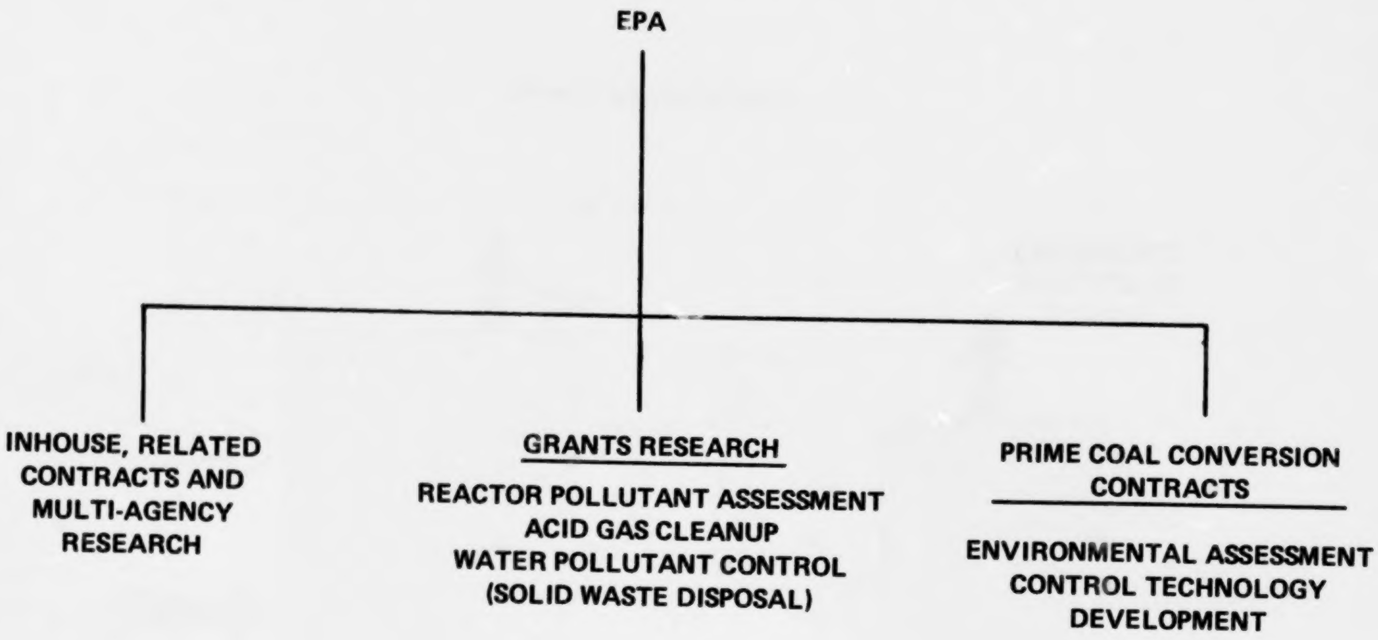
EPA
INHOUSE, RELATED CONTRACTS AND MULTI-AGENCY RESEARCH
GRANTS RESEARCH
REACTOR POLLUTANT ASSESSMENT
ACID GAS CLEANUP
WATER POLLUTANT CONTROL
(SOLID WASTE DISPOSAL)
PRIME COAL CONVERSION CONTRACTS
ENVIRONMENTAL ASSESSMENT
CONTROL TECHNOLOGY DEVELOPMENT

Figure 2. EPA program.

association of oncogenic activity with environmental causes is now widely accepted.

Increased environmental concern in the nation has necessarily extended into new areas of environmental problems. Improved chemical analytical techniques, which have made it possible to quantify substances at nanogram levels and parts per trillion concentrations, have influenced the increasing list of potential pollutants. Table 1 lists some potentially hazardous substances taken from an investigation of more than 200 substances.[1] These are grouped in terms of increasing hazard potential based upon both carcinogenic and toxic effects (it may be noted that some compounds, such as SO_2, are not included when considerations of *quantities* in the environment are ignored).

2. EPA recognizes that there are large information gaps concerning highly toxic substances associated with coal conversion. The problems, whether real or imagined, must be verified, or eliminated. Certainly, claims of environmental dangers associated with synthetic fuels which slow the progress of the industry must be addressed. A general example of the force of such claims is a settlement agreement resulting from litigation against EPA by various environmental organizations. The agreement sets a time table for new source performance standards, effluent guidelines and pretreatment controls for a list of more than 300 specific point source categories or industries. Commonly referred to as the Consent Decree,[2] this document now has been modified to include more than 100 substances which must be addressed for pollutant control.

3. Regulatory and standard setting processes are encompassing a larger number of pollutants. A new source performance standard under EPA review would designate control levels for sulfur species and hydrocarbons in the areas of coal gasifier lockhoppers, coal gas purification facilities, byproduct recovery, gas/liquid separation facilities, and sour water stripping facilities.[3] The fairly recent OSHA standard for hydrocarbon control in the vicinity of coke ovens (primarily concerned with carcinogenic activity) set an important precedent. This organization has also legally established threshold limits for about 500 different substances in the workroom atmosphere.[4]

4. Research on coal conversion reactors and associated toxic substances is considered an important factor in developing control technologies in these areas. Processes for direct burning of product gases from low Btu gasifiers, followed only by particulate cleanup, have been proposed. Both high- and low-Btu conversion processes often call for combustion of chars and tars for process heat and steam. These feedstocks must be analyzed to insure that incineration will accomplish complete destruction of hazardous materials.

The most important control option to be observed at the RTI experimental facility will be that of the reactor itself. The concept of utilizing the reactor for pollutant control through parametric variations is not an original one, but has received little previous development. The Environmental Protection Agency is interested in the idea of utilizing process variations or modification of process modules in order to effect environmental control. Where this is possible, of course, redundance and/or retrofitting of additional control systems is avoided. It is at the same time essential that any variations in process operation not severely limit production or result in unfavorable cost tradeoffs between process variation

TABLE 1

SUBSTANCES RECEIVING TOXIC INDICATORS

x	xx	xxx
2-Chloro-2,3-epoxypropane	N-Nitrosodimethylamine	4-Nitrobiphenyl
Formaldehyde	N-Nitrosodiethylamine	Dibenzo(a,h)anthracene
Acrolein	Ethyleneimine	Benzo(a)pyrene
Phthalic acid	Diazomethane	Alkyl Mercury
Monomethyl hydrazine	PCB's	Beryllium
Aminotoluenes	4,6-Dinitrocresol	Arsenic
2-Aminonaphthalene	Benz(a)anthracene	Arsine
4-Aminobiphenyl	Dibenzo(a,i)pyrene	Arsenic Trioxide
1-Aminonaphthalene	3-Methylcholanthrene	Selenium
N,N′Dimethylhydrazine	Tetramethyl lead	Chromium
α-Chlorotoluene	Thallium	Cadmium
1-Chloro-2-Nitrobenzene	Lead	Mercury
1-Chloro-4-Nitrobenzene	Hydrazine	
2,4-Dichlorophenol	Phosphorus	
2,4,6-Trinitrophenol	Phosphine	
Anthracene	Antimony	
Chrysene	Antimony Trioxide	
Dibenzo(b,def)chysene	Ozone	
Benzo(b)fluoranthene	Cobalt	
Pyridine	Nickel	
Dibenz(a,j)acridine	Silver	
Dibenz(a,h)acridine	Uranium	
Dibenz(c,g)Carbozole		
Tetraethyl lead		
Organotin		
Nickeocene		
PPAH (Collective)		
Lithium		
Lithium hydride		
Barium		
Germanium		
Bismuth		
Hydrogen sulfide		
Tellurium		
Vanadium		
Nickel carbonyl		

and simply adding control technologies.

5. Benefits may accrue through operation of a small and versatile system where a number of system variations can be assessed inexpensively. The bench-scale approach developed is quite flexible, allowing changes in the course of research where indicated to be profitable. This avoids the difficulties and expense incurred in attempting the same approach with a pilot- or full-scale unit and allows rapid response to reassessed needs and prior results.

6. Finally, some facets of this program mark a continuation of an earlier project supported by EPA in the area of reaction kinetics associated with coal conversion.[5] The main emphasis of this previous work was on desulfurization kinetics and involved a nonisothermal approach which will be followed up on a broader scale. This approach holds some promise and could produce at least some predictions of probabilities of formation for compounds of interest.

RESEARCH APPROACH

The research program is intended to progress in the three complimentary phases: screening studies, parametric control evaluations, and reaction kinetics research.

The first phase of efforts, screening studies, will be first associated with broad qualitative chemical analyses of a large number of compounds produced during gasification reactions. Attempts will be made to gasify a variety of U.S. coals through a range of reactor conditions, primarily to provide the opportunity for production of practically any substance which might be associated with gasification. It is probable that up to 300 different compounds will be screened following many of these tests. Qualitative screening, which will emphasize detection of the presence of the higher molecular weight organics already mentioned and particular compounds designated as having high toxic potential. The screening will also produce relative quantifications for selection of particular compounds that are present in gross enough quantities to warrant further investigation. Work will also be concerned with the isolation of chemical groups, such as polynuclear aromatics.

Screening studies will then move into the quantitation of selected compounds which, because of their relatively high concentrations balanced with their health hazard potential, are specified as important gasification pollutants. Confidence in this approach will be built through reproduction of the same substances under similar conditions while utilizing more specific and rigorous analysis.

Figures 3a and 3b (Figure 3a is an overlay) demonstrate one approach for estimating the amount of sample which must be taken from the products or byproducts from the gasifier to insure that possibly hazardous pollutants have been detected at levels which may be environmentally significant. Parameters taken into consideration include:

1. For a full scale plant—average stack heights, average wind speeds and weather conditions within the U.S. (primarily based on the states with high coal reserves), plant production (a 20,000 ton/day of coal plant was considered here), and a maximum concentration for any specific pollutant calculated using a dispersion model.

2. For the experimental setup—test duration, amount of coal input, duration of the sampling period (variable), and the percent of product/byproduct stream sampled during the same period (variable). The latter were multiplied to form a composite variable.

3. For the potential pollutants—an estimated permissible concentration (variable) has been derived for over 200 potential pollutants from fossil fuel processes.[1] Parameters involved in the derivation of these permissible concentrations (which in this case only included EPC's for ambient air considering effects on human health) were threshold limit values, LD_{50}'s and

Benzo(a)pyrene

Dibenzo(a,h)anthracene

3-Methylcholanthrene

Dibenzo(a,i)pyrene
Alkyl mercury
9,10-Dimethyl-1,2-benzanthracene

1-Chloro-2,3-epoxypropane
Acrolein
Aminotoluenes
2-Aminonaphthalene
1-Aminonaphthalene
Ethyleneimine
Diazomethane
Monomethyl hydrazine
N-Nitrosodimethylamine
N-Nitrosodiethylamine
4,6-Dinitro-O-cresol
2,4,6-Trinitrophenol
Naphthalene
Anthracene
Phenanthrene
Naphthacene
Benz(a)anthracene
Benzo(c)phenanthrene
Chrysene
Methyl chrysene
Triphenylene
Pyrene
Dimethyl pyrenes
Benzo(g)chrysenes
1,2,3,4-Dibenzanthracane
Benzo(e)pyrene
Perylene
Picene
Dibenzo(b,def)chrysene
Dibenzo(a,l)pyrene
Benzo(ghi)perylene
Coronene
Fluorene
Benzo(b)fluoranthene
Acridine
Dibenzo(a,j)acridine
Dibenz(a,h)acridine
11 H-Indeno(1,2-b)quinoline
Dibenzo(c,g)carbazole
Tetramethyl lead - Tetraethyl lead
Organotin

Formaldehyde
Tetramethylsuccinonitrile
4-Aminobiphenyl
N,N'Dimethylhydrazine
N,N-Dimethylhydrazine
Methyl mercaptan
Ethyl mercaptan
N-Butyl mercaptan
Biphenyl
1,4-Dichlorobenzene
PCB's
a-Chlorotoluene
Dinitrotoluene
Dinitrophenols
1-Chloro-4-nitrobenzene
Pyrrole
Thiophene
Copper-8-hydroxyquinoline

2,2'-Dichlorodiethyl ether
Phenylethanol
t-Pentanol
Ethylene glycol
Propionaldehyde
Isophorone
Formic acid
Acetic acid
Phthalic acid
Formamide
Phthalate esters
Benzonitrile
Cyclohexylamine
Aniline
4,4'-Diaminodiphenyl
Butylamines
Ethanolamine
Ethylamine
Dimethylaniline
Dimethylamine
N,N-Dimethylaniline
Hydrazobenzene
Benzenesulfonic acid
Benzene
Nitrobenzene
1-Chloro-2-nitrobenzene
Nitrotoluenes
Phenol
Cresols
Xylenols
Catechol
2-Chlorophenol
2,4-Dichlorophenol
3-Nitrophenol
4-Nitrophenol
Pyridine
Picolines
Quinoline
Isoquinoline
2-Methylquinoline
Benz(c)acridine
Indole
Carbazole
Dibenz(a,g)carbazole
Methylthiophenes
Benzo(b)thiophene
Ferrocene
Nickelocene

Methyl chloride
1,4-Dioxane
Methanol
Butanols
Pentanols
t-Butanol
Acetaldehyde
Butraldehyde
Benzaldehyde
Benzoic acid
Hydroxy acetic acid
Acetonitrile
Acrylonitrile
Toluene
Tetrahydronaphthalene
Chlorobenzene
1,2-Dichlorobenzene
2-Chlorotoluene
Phenylphenol
Indanols
2-Nitrophenol
Indan, Indene
Collidines

Figure 3a. Compounds ordered on basis of EPC and sampling required.

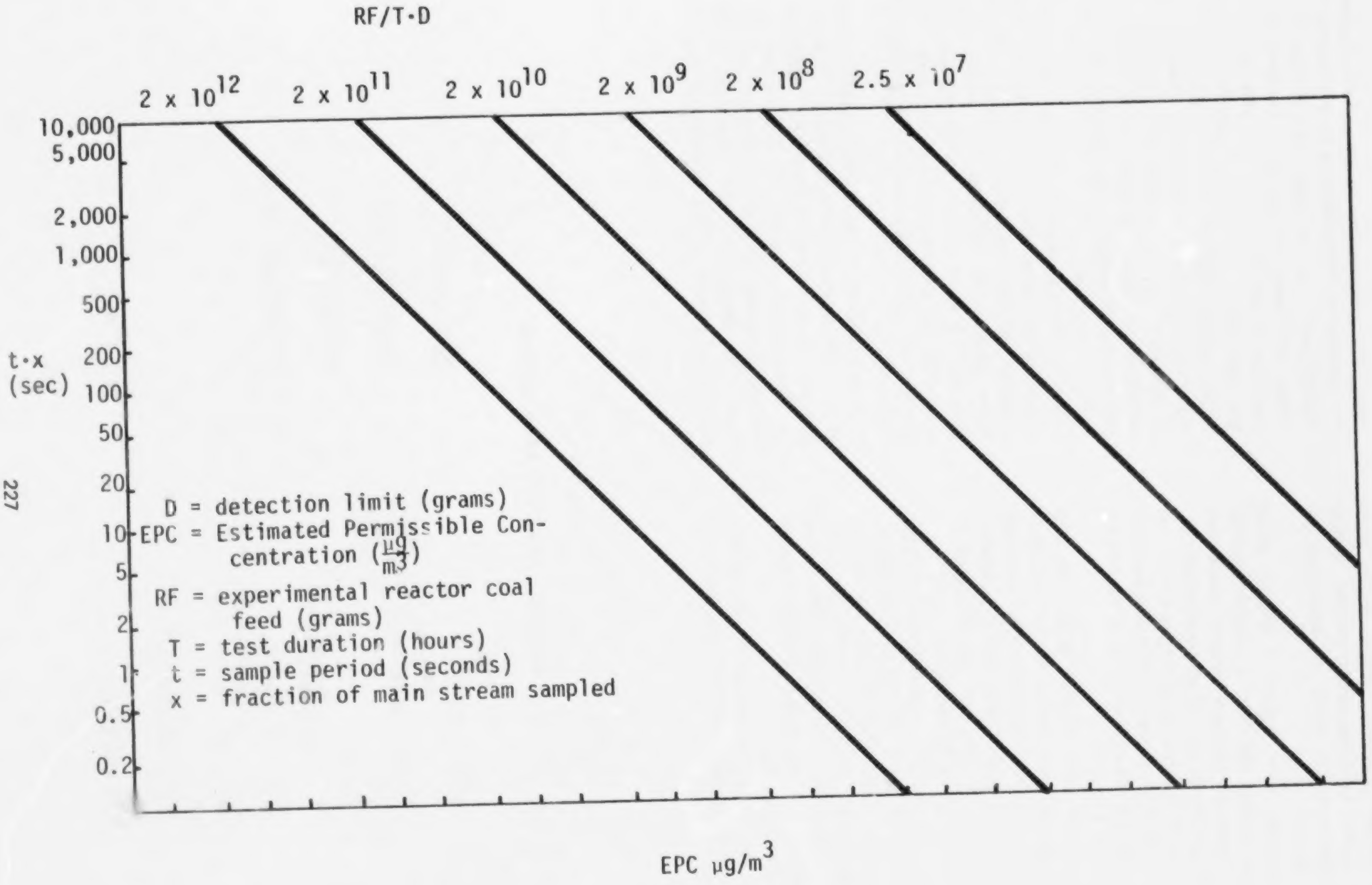

Figure 3b. Sampling required for proper environmental assessment.

human breathing rates, or in some cases, carcinogenic potential, human consumption rates, or ecological effects.

The overlay with Figure 3 shows those pollutants which fall into a specific sampling—i.e., sample percent ranges associated with their particular estimated permissible concentrations. These sampling ranges are further subdivided by the parameters of the experimental tests that are possible with the RTI synthetic fuels reaction system.

An important part of both qualitative and quantitative screening will be the development of improved analytical techniques for analysis of coal conversion products and byproducts. (Developments to date will be discussed in another paper at this Symposium.)

Throughout testing, quantitative measurements will be made on-site of fixed gases, sulfur species, and hydrocarbons up to C_6. These analyses will be made by gas chromatograph and, at a later date, continuous gas monitors for the major product gases associated with gasification.

The second phase of research, concerned with parametric studies, involves application of the gasification reactor to the control of potential pollutants. Parameters to be considered for investigation include those listed in Table 2. To these could also be added the parameters of bed type (fixed, entrained, fluidized) and reactor type (batch, semibatch, plug flow, mixed flow) which should receive attention as research progresses. A statistical approach for optimization of parametric combinations to minimize the number of tests required while investigating all possible influences is currently being undertaken.

Results from parametric testing will be continuously compared with those from chemical analyses so that influential variables can be more extensively assessed as testing progresses. It is obvious that, unless the test plan is directed by previous engineering data , the number of tests could burgeon to orders of 10^3-10^4.

Other researchers[6] have noted the influence of different reactor configurations on the production of byproducts of possible environmental significance. Results of this nature are scarce, however, and extrapolations are difficult. The literature[7,8,9,10,11] describes some established effects of the variation of reactor

TABLE 2

POSSIBLE REACTOR PARAMETERS

COAL TYPE

GRIND SIZE

GASES
  COMPOSITION
  FLOW RATE

STEAM

PRETREATMENT

CATALYST

BED DEPTH

TEMPERATURE

PRESSURE

RESIDENCE TIMES

conditions on major gasification kinetics. Some examples follow:

Pretreated chars may be several orders of magnitude less reactive in terms of oxidation than raw or mildly pretreated coals. The rate of the endothermic reaction

$$C + H_2O \rightarrow CO + H_2$$

varies widely for different coals. Char-CO_2 gasification and hydrogasification contribute little to coal conversion in low pressure steam/oxygen gasifiers. High temperatures favor CO production in the exothermic water-gas shift reaction, while hydrogen is more evident at lower temperatures. Conversion of coal sulfur to gaseous species is a rate-limited phenomenon, and is generally promoted by conditions that lead to high carbon conversion. Product distribution through pyrolysis or volatilization is a strong function of both the final reaction temperature and the time taken to reach it. For example, at high heating rates on the orders of 10,000-50,000° C/s—rates typically attained in continuous fluidized bed and entrained bed gasifiers—the yield of volatiles at a given temperature and the tar-to-gas ratio of the product are both higher than at lower heating rates. Packed beds, larger particles, and elevated gasifier pressures tend to diminish yields of tar and augment yields of char and light hydrocarbon gases during pyrolysis. Observations indicate that char, in general, is less reactive than carbon in nondevolatilized coal in reaction with such species as steam, oxygen, or hydrogen.

Another factor, which can be particularly important in an experimental nonproduction system such as the RTI reactor, is that of nonsteady state conditions. Also, steady-state production of major gases (CO_2, CO, H_2, CH_4) is not an assured indication of a steady output of trace constituents.

Possible relationships of formation probabilities to process parameters will be further evaluated in the kinetics phase of the RTI studies. Some tests in this phase will include:

1. Development of analytical methods,
2. Ascertaining appropriate level of stratification of pollutants,
3. Conducting experimental nonisothermal tests, and
4. Reduction, tabulation, and analysis of data and application to pollutant reduction.

Data obtained through the nonisothermal measurement technique is applicable to any chemical reaction. Nonisothermal techniques are somewhat controversial, and options for reverting to isothermal studies will be retained. In the analysis of coals and coke, nonisothermal measurements are advantageous because, in isothermal studies, the large effect of heating to a given reaction temperature is controlling the competing reactions and consequently the results. For the nonisothermal method, the reaction rates are to be studied at a preprogrammed rate of heating of the solid samples.

Figure 4 depicts the reaction velocity constants for the decomposition of hydrocarbons and petroleum fractions associated with petroleum refining. On this figure is superimposed the typical reaction velocity curve as a function of temperature obtained from some previous studies utilizing nonisothermal reaction kinetics. It is obvious from this simple example that if the reaction velocity can be obtained as a function of temperature, the operating conditions can be selected to favor the desired reactions and to minimize the undesired ones.

One theoretical procedure for obtaining changing concentration (for first order kinetics) as a function of temperature is given in equations below.

$$\frac{dV}{dT} = k_o \left[\exp - \frac{E}{RT} \right] (V_f - V)$$

$$\text{If } \frac{1}{T} = X, \; -dt = dX$$

$$dt = -\frac{1}{T^2}\, dT$$

$$t = \frac{1}{T} + c$$

$$T = \frac{1}{t-c} = \frac{K}{t_{max} - t}$$

$$\frac{dV}{V_f - V} = -k_o \exp\left(-\frac{E}{R} X\right) dX$$

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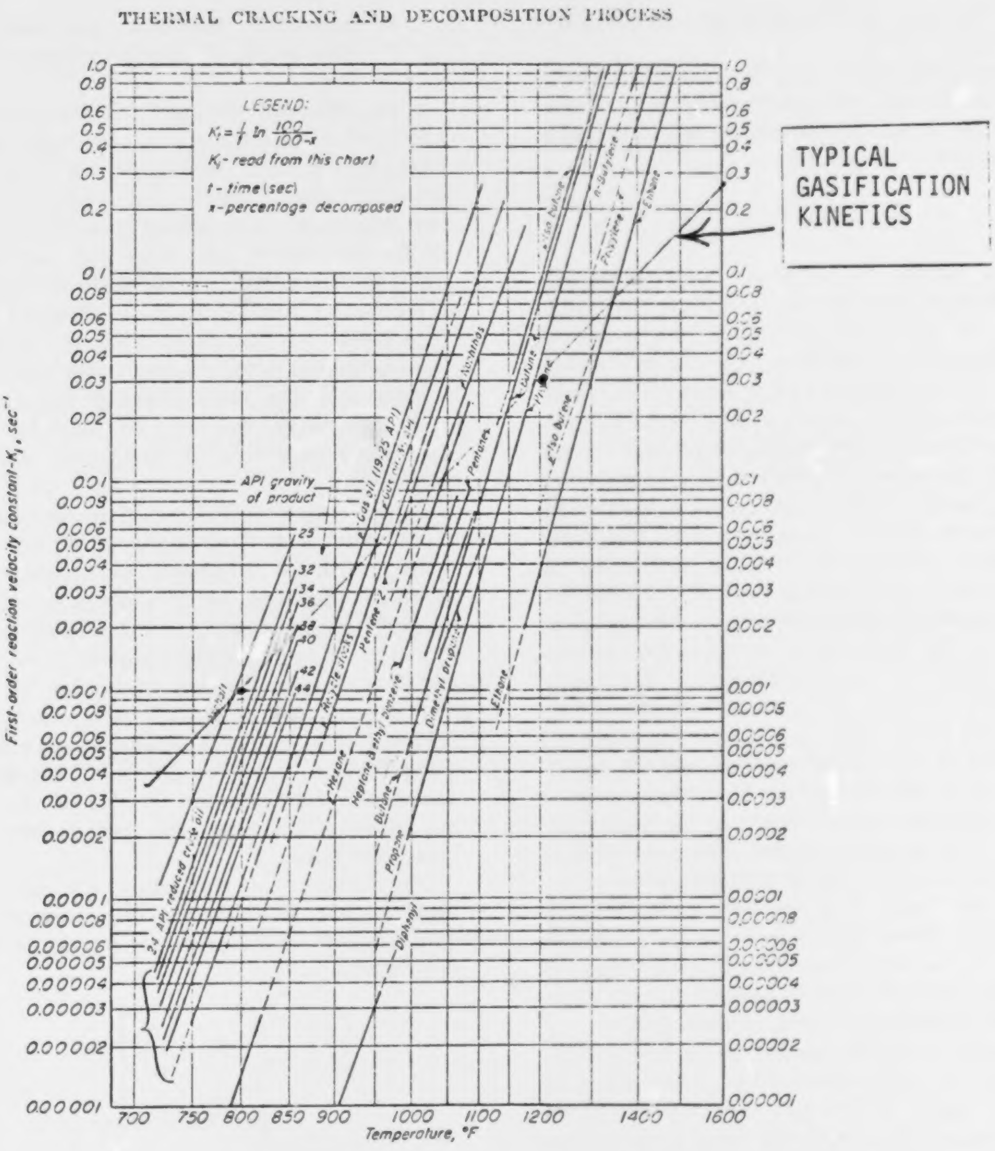

$$K = 1.6 \times 10^{13}/\text{sec} \quad \exp - \frac{55{,}000 \text{ cal}}{RT - {}^{\circ}K}$$

Figure 4. Reaction velocity constants for the decomposition of hydrocarbons and petroleum fractions into various products.

$$\ln \frac{V_f - V}{V_f} =$$

$$-\frac{k_o R}{E} \exp\left(-\frac{E}{R} X\right)\Bigg|_{\infty}^{1/T} = -\frac{k_o R}{E}\left[\exp - \frac{E}{RT}\right]$$

$$\ln\left[-\ln \frac{V_f - V}{V_f}\right] = \ln \frac{k_o R}{E} = -\frac{E}{RT}$$

This approach, properly conducted, permits the simultaneous determination of the sets of two parameters in the typical Arrhenius expressions for the reaction velocity constants for pollutants of interest. An example of a plot for a first order test is shown in Figure 5.

Knowledge of the kinetics of formation can be utilized to suggest changes in the operating conditions of a synthetic fuels conversion system to minimize pollutant formation. Such changes can then be confirmed, for example, on the RTI gasifier. The results from the use of chemical reaction theories will be related to the corresponding experimental and chemical analytical studies.

Although the thermodynamics and kinetics of coal pyrolysis, gasification and desulfurization have received attention, these areas are still not well defined. Complexities of the materials and the reactions involved make a unifying theory most elusive. Descriptions of

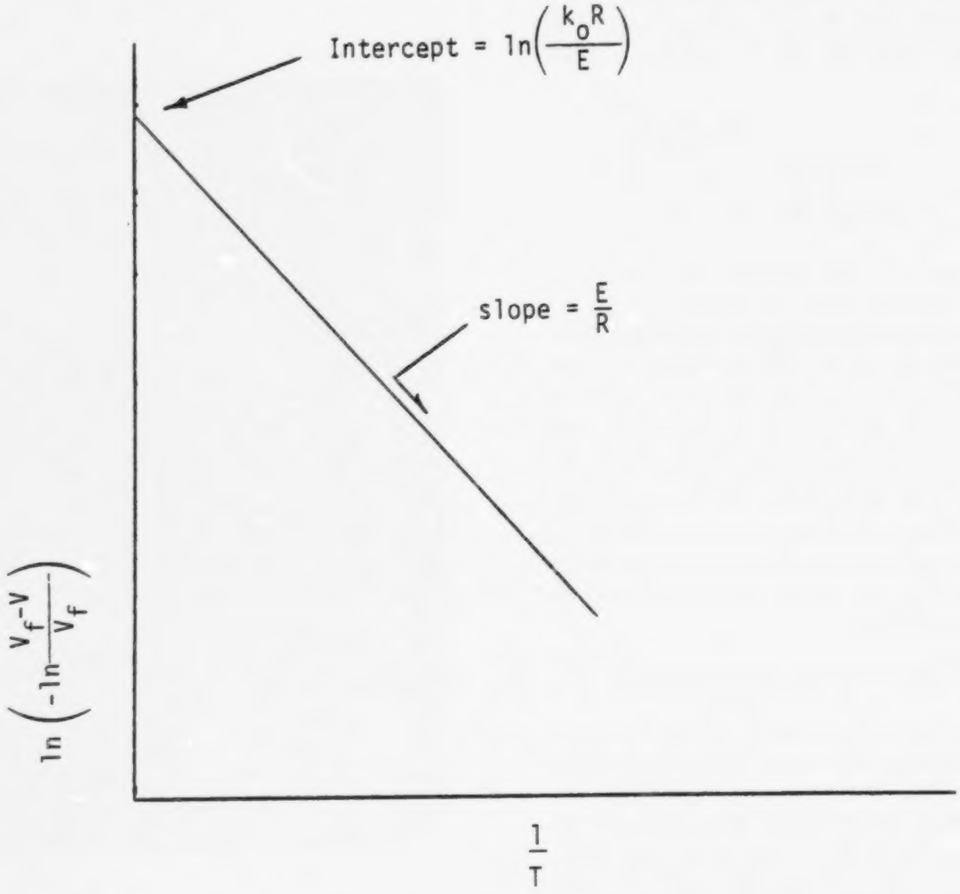

Figure 5. First-order test plot.

devolatilization have, for the most part, treated the combined volatile fractions. This necessitates such approaches as Gaussian distribution estimation of the activation energies, semi-empirical results for determining rate constants, mean activation energy and standard deviations, and some rather complicated rate expressions. Devolatilization rate may be controlled by kinetics or mass and heat transfer, and the product distribution is often provided by coupled effects. Also, reactive volatile products such as tars may undergo secondary cracking or polymerization reactions.

For gasification, mechanisms and rates of the reactions involved have been postulated. Rate laws of the Langmuir type and also more simplified forms have been proposed for the primary carbon/steam mechanism. Van-Fredersdorff and Elliott[7] have proposed a Langmuir-Hinselwood rate law given by equation

$$r = \frac{\left[k \quad PH_2 \, PCO_2 - \frac{PCO \, PH_2O}{k}\right]}{1 + K_A PCO_2 + K_R PCO}.$$

Wen[12] uses a simpler form of the rate law, a reversible second order expression.

A literature survey has been carried out to explore these and other efforts describing coal gasification kinetics, including the reactions leading to the generation of H_2S, CS_2, and COS. While these studies provide some exemplary approaches to solving reaction kinetics problems, it is recognized that the same approaches may not be applicable to formations of trace constituents of interest and that indeed problems involved in the latter effort may be much more difficult.

IMPLEMENTATION OF APPROACH

The unique requirements of the program have demanded extensive additions of hardware, facilities, and analytical equipment. The opportunity of close coordination with the Environmental Protection Agency and familiarity through previous programs with the environmental problems of coal conversion processes have facilitated progress.

Attempts have been made initially to avoid as many problems as possible. Initial testing will investigate the gasification area of fossil fuels conversion only. A simple experimental system has been devised that is much less complex than a full-scale plant design yet, hopefully, offers good approximation of the reactor operation of such facilities.

The coal conversion reactor, Figure 6, topped by the tubular coal feed hopper, extends only approximately nine feet in height. Under operating conditions, the reactor is encased in a vertical furnace which allows preheat of internal inert gases or reactor wall heating of the coal bed and gases during reaction.

The reactor operates in a semibatch mode—i.e., the entire charge of coal to be gasified is injected into the reactor, and steam,

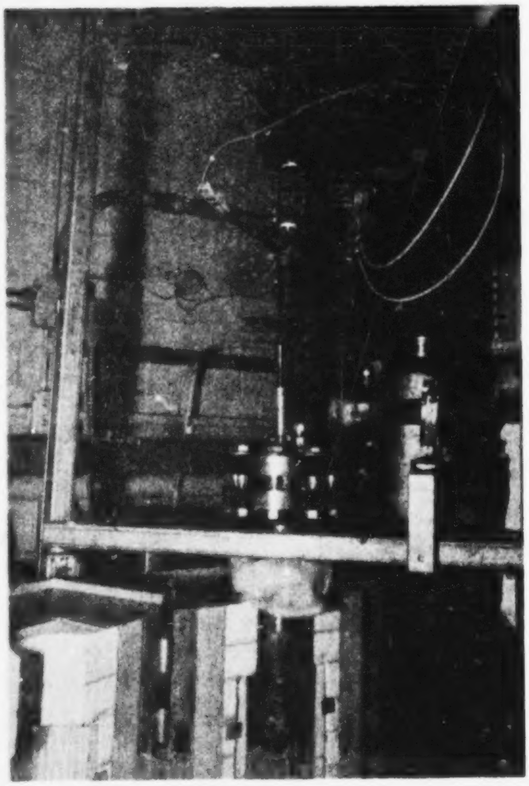

Figure 6. Gasification reactor.

along with other gases, is continuously passed through the bed during a test run. Such an approach obviously relieves the experimental work of the complications of continuous coal feed and ash/char removal. Consequently a porous,temperature-resistant ceramic flow distributor, Figure 7, which supports the coal bed in the reactor itself, is situated in the reactor. This allows a reasonably homogenous fixed bed or, on the other hand, a truly fluidized bed as opposed to many of the suspended or highly entraining beds associated with many pilot-scale processes. The flow distributor is designed to eliminate channeling around the circumference and to present a pressure drop conducive to optimized fluidization should the reactor be operated in this mode.

Coal beds in the reactor are fixed at present. It is hoped that reasonable results and simulations can be obtained with fixed bed reaction since this will eliminate the modeling difficulties associated with fluidized beds, e.g., bubbling. The primary concern is to simulate the reaction history of coal particles introduced into gasification reactors, particularly those phases which might be most closely associated with the production of contaminants. These phases include (1) surface evaporation of volatiles—probably zero order, low activation energy; (2) diffusional evaporation of volatiles—probably first order, low activation energy; (3) surface cracking—complex order, high activation energy; and (4) organic sulfur decomposition and removal—two ranges, first order, high activation energy. A comparison of the differences between continuous and batch feed in terms of coal particle history and reaction analysis is given in Table 3.

While investigating some of the fundamental questions associated with the possible production of toxic materials in this experimental gasifier, it is at the same time essential that the experimental procedures offer a real approximation of gasification processes which exist or

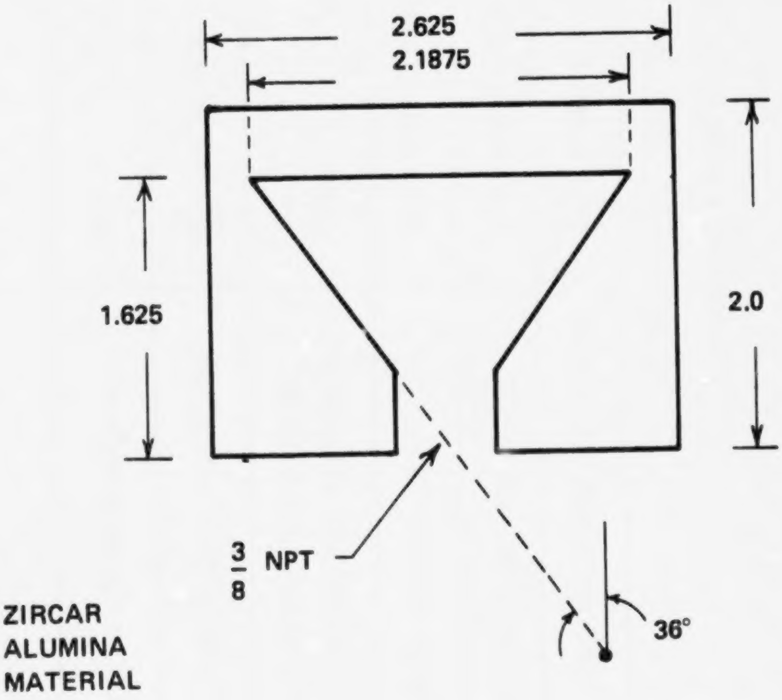

Figure 7. Flow distributor

TABLE 3

COMPARISON OF REACTOR CHARACTERISTICS

	BATCH	CONTINUOUS
FEED MATERIAL REQUIRED	ONE REACTOR VOLUME	MANY REACTOR VOLUMES
LENGTH OF RUN	ABOUT 1 REACTOR TIME	MANY REACTION TIMES
BEST APPLICATION	EXPERIMENTATION	PRODUCTION
INDEPENDENT VARIABLE (CHEMICAL REACTIONS)	TIME	DISTANCE; AND TIME UNTIL STEADY STATE
TYPICAL RATE EQUATION	$\frac{dc}{dt} = K[T(t)]\,c(t)$	$u\frac{dc}{dx} = K[T(x)]\,c(x)$
USUAL MEASUREMENTS	$c(t)$	c at $x = o$; $x = L$

have been proposed for operation in the United States. The laboratory gasifier has been designed to cover a wide range of operating conditions to provide some simulation of large-scale gasifiers. Mass ratios of gases or steam to coal ratios, internal pressures, reactor gas and coal bed temperatures, bed types, particle sizes, and other parameters can be matched. The reactor is presently intended to gasify up to two kilograms of coal (noncaking or pretreated coals), and operate in pressure ranges from ambient to 1,000 psig (depending upon temperature) and temperatures to 1950° F. Nominal testing ranges at present are 200-300 psig, maximum temperatures to 1900° F, and coal masses of less than one kilogram.

All gas flow and pressure control is maintained at a single control panel. Steam generation and steam superheating to injection temperatures (up to 1500° F) are accomplished through a series of remotely controlled furnances fed by high-pressure, low-flow metering pumps.

Temperature control within the reactor itself is accomplished in one of two ways:

1. Controlling the level of oxygen flow and, therefore, combustion within the coal bed, and/or
2. Varying current supply to the remotely controlled vertical furnace and a separate strip heater near the top flange of the reactor.

Internal temperatures are measured in the reactor in the axial direction during testing. Vertical temperature gradients scheduled for observations are quite possibly an important parameter in the generation of particular gasification contaminants. Provision has been made for remote control of the three zones of the vertical furnance utilizing a Datatrack programmer. This allows graphical inputs describing a desired temperature profile to be followed during test runs. Therefore, during nonisothermal kinetic studies, a temperature profile can be selected to eliminate nonlinearities in the solutions to proposed rate equations and allow simplified extrapolation and solution for rate constants and activation energies.

An operational schematic of the mechanics of the experimental laboratory gasifier system is shown in Figure 8.

Product gases from the gasifier pass through a series of traps designed to eliminate particulates, tars, water, and other condensates before the gases pass to the gas sampling train. Substances remaining in the traps are analyzed primarily by GC/mass spectrometry and high pressure liquid chromatography.

The RTI sampling train in use at present is shown in Figure 9. Discrete gas samples are currently being taken for on-site analyses by gas chromatography of fixed gases (N_2, O_2, CO, CO_2), sulfur species (e.g., H_2S, COS), and hydrocarbons (less than C_6). On-site continuous gas monitors will be added in the near future for fixed gases and methane. This is, of course, most important to assure reasonable simulations by the laboratory reactor of real gasification processes. Heavy organics and other constituents are being adsorbed by XAD_2 and Tenax cartridges. The XAD_2 cartridges are sufficiently large to allow passage of the entire product gas stream through them throughout a test to provide an integrated sample of all contaminants, while the Tenax cartridges are valved to be individually selectable so that sampling may also be associated with discrete test times.

The sampling system is presently constructed of stainless steel. A glass sampling system is being planned.

All sampling and analysis areas are contained under ventilated hoods. The entire reactor facility area has been well ventilated to prevent worker exposure to hazardous contaminants.

An on-site signal processing unit has been included to manage both the large amount of data from the numerous sensors included in the experimental system and that data from on-site chemical analysis. This unit includes a 64 K core with compatible disk storage. Real time functioning is included which will allow reactor and sampling system control, automatic safety shut-off and on-line analysis during test periods. All data will be processed, stored, and analyzed through this system. The signal processing unit is backed up by multipoint and analog strip chart recorders and digital displays.

INITIAL TESTING

Experimental evaluations have just begun using the reactor system. A period of pregasifica-

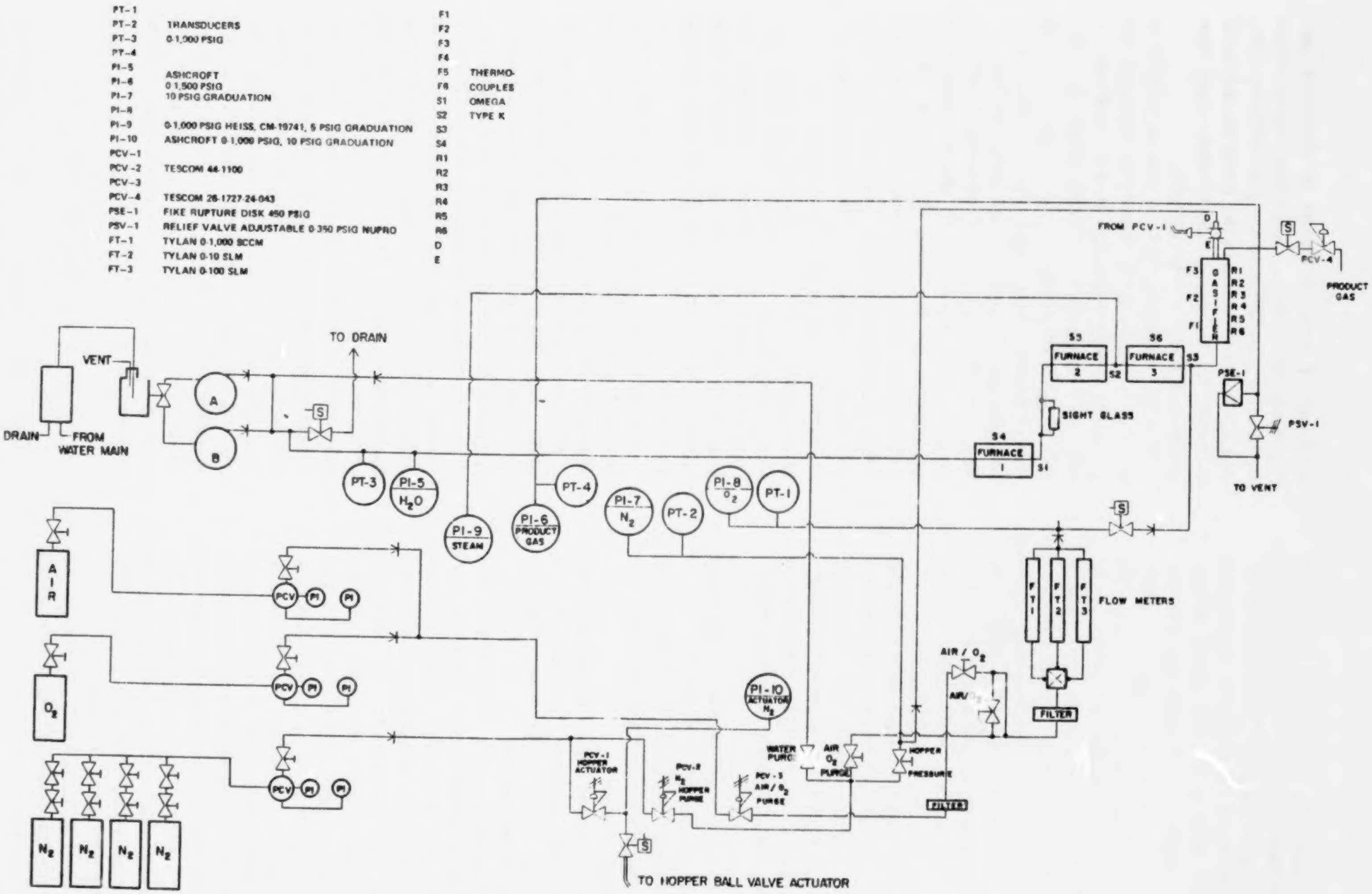
PT-1
PT-2 TRANSDUCERS
PT-3 0-1,000 PSIG
PT-4
PI-5
PI-6 ASHCROFT
PI-7 0-1,500 PSIG
10 PSIG GRADUATION
PI-8
PI-9 0-1,000 PSIG HEISS, CM-19741, 5 PSIG GRADUATION
PI-10 ASHCROFT 0-1,000 PSIG, 10 PSIG GRADUATION
PCV-1
PCV-2 TESCOM 44-1100
PCV-3
PCV-4 TESCOM 26-1727-24-043
PSE-1 FIKE RUPTURE DISK 450 PSIG
PSV-1 RELIEF VALVE ADJUSTABLE 0-350 PSIG NUPRO
FT-1 TYLAN 0-1,000 SCCM
FT-2 TYLAN 0-10 SLM
FT-3 TYLAN 0-100 SLM
F1
F2
F3
F4
F5 THERMO-
F6 COUPLES
S1 OMEGA
S2 TYPE K
S3
S4
R1
R2
R3
R4
R5
R6
D
E
VENT
DRAIN
FROM WATER MAIN
A
B
S
TO DRAIN
PT-3
PI-5 H2O
PI-9 STEAM
PI-6 PRODUCT GAS
PT-4
PI-7 N2
PT-2
PI-8 O2
PT-1
AIR
O2
N2
N2
N2
N2
PCV
PI
PI-10 ACTUATOR N2
PCV-1 HOPPER ACTUATOR
PCV-2 N2 HOPPER PURGE
PCV-3 AIR / O2 PURGE
WATER PURGE
AIR O2 PURGE
HOPPER PRESSURE
FILTER
TO HOPPER BALL VALVE ACTUATOR
AIR / O2
AIR/O2
FILTER
FT1
FT2
FT3
FLOW METERS
S4
FURNACE 1
S1
SIGHT GLASS
S5
FURNACE 2
S2
S6
FURNACE 3
S3
F1
F2
F3
GASIFIER
R1
R2
R3
R4
R5
R6
D
E
FROM PCV-1
S
PCV-4
PRODUCT GAS
PSE-1
PSV-1
TO VENT

Figure 8. Process schematic

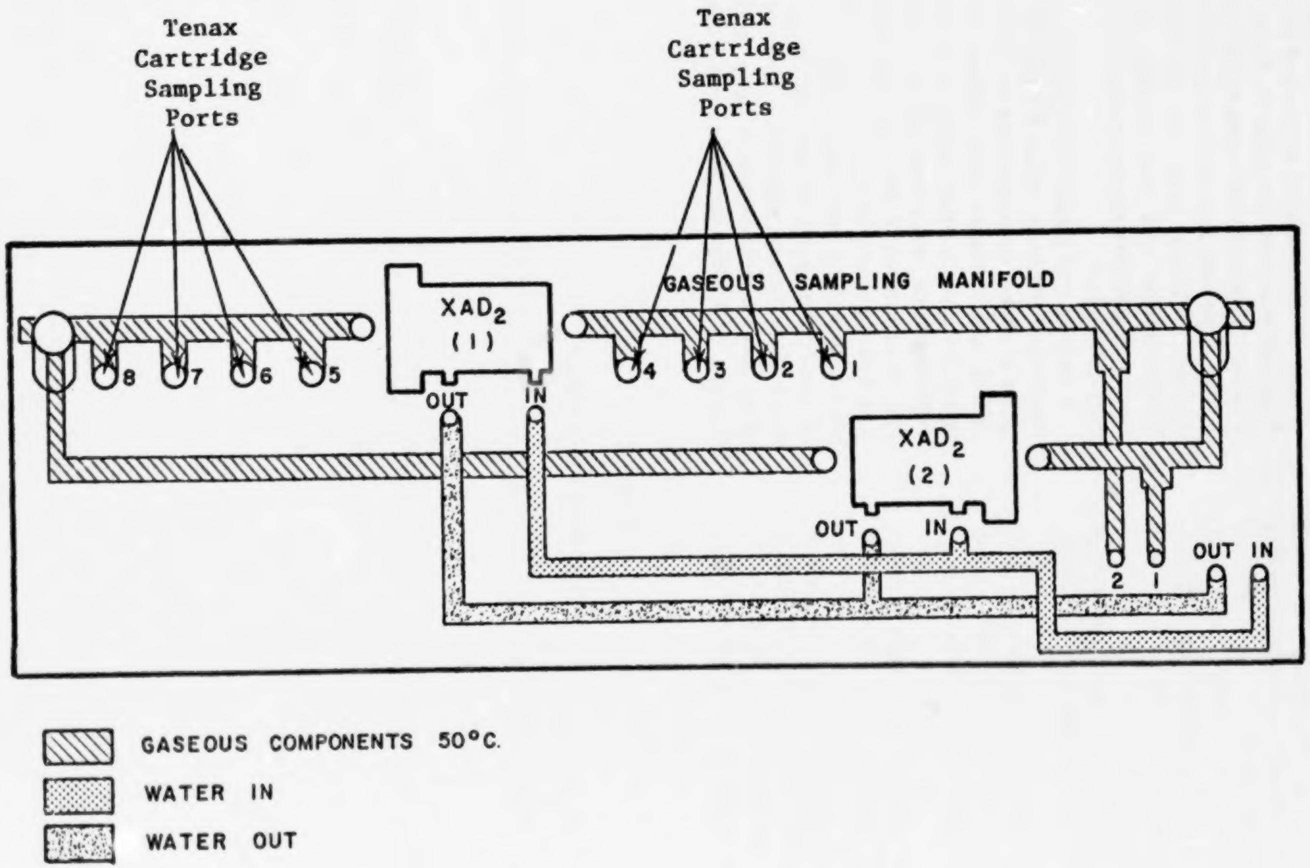
Tenax
Cartridge
Sampling
Ports
Tenax
Cartridge
Sampling
Ports
GASEOUS SAMPLING MANIFOLD
8
7
6
5
4
3
2
1
XAD$_2$
(1)
OUT
IN
XAD$_2$
(2)
OUT
IN
2
1
OUT
IN
GASEOUS COMPONENTS 50°C.
WATER IN
WATER OUT

Figure 9. Gaseous sampling manifold.

tion testing has included the following:

1. Calibrations of pumps, flow meters, thermocouples, pressure transducers, gas chromatographs, temperature controllers, digital displays, strip chart recorders, furnace responses, gauges and metering valves.
2. Heat up tests for steam generation, reactor internal temperature control, and particulate, tar and condensate trap temperature control.
3. Overall system flow tests using inert gases, and pressurization of all system modules.
4. Evaluation of radial temperature profiles within the reactor at various gas flow rates and flow distributor positions.
5. Fluidization tests in a plexiglass "reactor" with various coals of different mesh sizes.

The first reactor tests have been carried out primarily to ascertain the proper functioning of the system and the logistics of the sampling and analysis techniques. To facilitate matters, a Western Kentucky FMC char, low in volatiles and free-swelling index, has been used. A first test took a 175-gram sample of this char to nearly complete combustion with about 43 grams of ash remaining at the end of the test. Char-ash analyses are given in Table 4. Both air/coal and steam/coal mass ratios were near 1:1 to begin with and, air flow was increased at discrete intervals over the two-hour test. Temperatures did not exceed 800° C. Chemical analyses were not done for the products of this test.

A second test included much less complete reaction of the char, about 67 percent. Some gross chemical analyses done on the products of this test indicated lower carbon monoxide and higher hydrocarbon yields, which would be expected to be associated with the lower reaction temperatures of this test. Gas production was still increasing at the end of the sampling period, indicating that steady state conditions for gasification were not reached. Results from these tests remain qualitative, and more detailed assessment remains to be done. One indication from these and other tests is that inter-

TABLE 4

CHAR/ASH ANALYSES

Analyzed For	Char Sample Air	Ash Sample A1C
BTU/lb.	11,090	570
Moisture, %	1.0	0.9
Ash, %	19.7	91.0
Volatile Matter, %	7.8	6.9
Fixed Carbon, %	71.5	1.2
Sulfur, %	1.8	0.2
Carbon, %	74.02	13.82
Hydrogen, %	1.48	0.82
Oxygen, %	1.7	<0.1
FSI	<1.0	<1.0
Ash Fusion Temp.	2,600	2,610
Nitrogen (TKN), %	1.3	0.3

nal reactor temperatures could be reasonably controlled by varying power input to the surrounding vertical furnace. Therefore, a more recent experiment investigated gasification of a small amount of char, 175 grams again, in the absence of combustion.

This last experiment was carried out utilizing the Datatrack programmer to provide a ramp function for control of vertical furnace temperatures. Furnance and reactor temperatures were initially increased to approximately 700° C before char was injected into the bed. Steam was continuously passed through the bed following injection. Steam flow was supplemented by a carrier gas (N_2) to improve flow and temperature stability of the injected steam.

It has been demonstrated in all tests that heat conduction and gas flow convection through the bed allow reasonably short heat-up times to increase char bed temperatures to those originally in the preheated reactor. Increased flow through the bed has been demonstrated to shorten this heat-up time. Internal reactor and coal bed temperatures were also demonstrated in the last mentioned test to closely follow the signal input for signal temperature control from the Datatrack program. These results are shown in a general fashion in Figure 10.

Few problems have been encountered to date in this simple and low risk system design. Some recognized problems, however, have included the difficulty of flow control at very low rates (for example, less than 1 standard liter per minute) and high pressures, placement of the flow distributor within the reactor which will completely prevent channeling and consequent oxygen breakthroughs, coordination of metering valve controls with back pressure regulation at very low gas flow rates, placement of sufficient thermal insulation in small spaces where high heat losses are possible, maintaining upper reactor temperatures to prevent condensation of exit gases before passage through the proper traps, and maintaining superheat steam temperatures at very low flow rates. Most of these problems have been solved, all or in part.

PLANNED RESEARCH

During the final quarter of the first year of research, several brief tests are planned which are concerned with improving system controllability as indicated by results from early gasification tests. Reevaluation of system components is also being carried out.

As soon as confidence has been developed in the capability of the RTI reactor to provide reasonable simulation of coal gasification characteristics, a second phase of gasification testing will be entered. Different coals and reactor parameters will be used, and extensive screening evaluations of all products and byproducts will be carried out. Intentions are at this time to begin with a representative eastern coal (e.g., Kentucky, Illinois, or Pittsburgh). This coal will be of a reasonably large mesh size such as the 10 by 80 char size used to date.

Testing on the eastern coal will be followed by gasification of a western subbituminous coal such as Montana Rosebud. Again, a large mesh size will be used. Both coal samples will be gasified during separate tests at two different temperatures. Future comparisons will be made with real gasification processes.

Further tests will be carried out using smaller mesh sizes. This will be done first to evaluate the coal supply system with these sizes, secondly to investigate bed flow through or fluidization problems, and finally to examine the effects upon pollutant production.

All future plans are dependent upon directions from the Environmental Protection Agency. Some likely improvements will include in-house coal preparation including grinding and screening and possibly in-house sample analyses to include proximate, ultimate, and more intensive analyses. It was mentioned previously that continuous gas monitors will be added to give real time assessment of product gases. A number of safety features and alarms are planned. Preliminary investigations have been begun into utilizing gamma ray detection for measurement of fixed or fluidized bed levels within the reactor. Hopefully, in-house pretreatment of caking coals will be added.

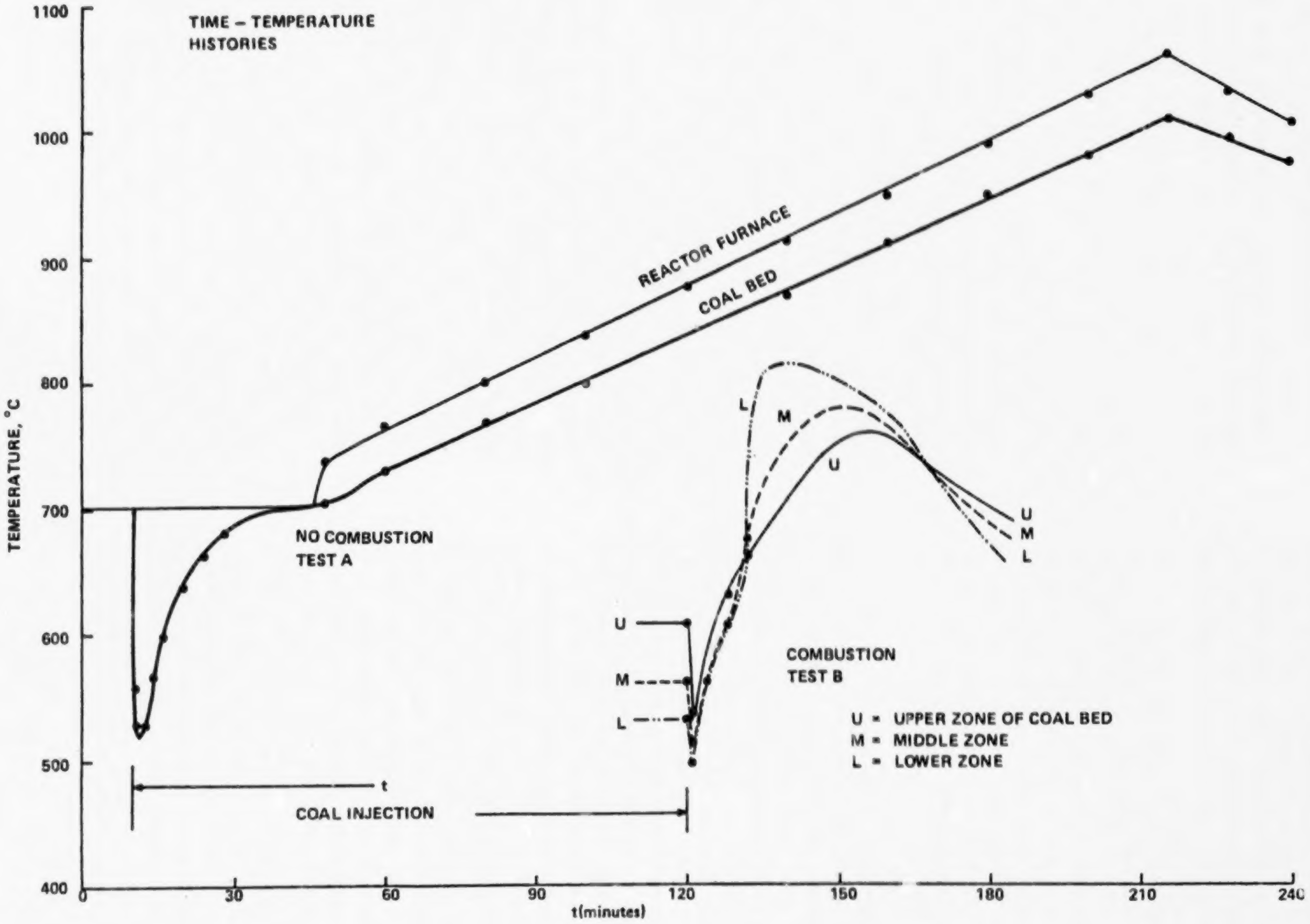

Figure 10. Early gasification tests.

Some extensions of the research discussed which seem potentially valuable:

1. Simplified experimental reactions to provide better correlation with theoretical analyses, e.g., reaction of thin coal wafers to provide a one-dimensional approximation and the observation of the action of very small coal samples in conjunction with thermogravimetric analysis tied to continuous mass spectromery.
2. Investigation of byproduct or contaminant production following the incineration of gasifier tars and chars.
3. Continuous coal feed to the reactor to evaluate discrepancies produced by this method with the results obtained during batch operations.
4. Determination of the effects of fluidization and entrainment on the production of toxic or other trace constitutents presenting health hazards.
5. Comparison of contaminants analyzed for and samples taken from different regions of the coal conversion reactor.

It is hoped that the present and future research plans described will begin to produce some profitable scientific results in the upcoming year and be made available to those interested in coal conversion. It is also hoped that these results will alleviate concern over environmental problems associated with coal utilization.

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GASIFICATION PROCESS/ ENVIRONMENTAL CHARACTERIZATION FROM PILOT PLANT DATA

by

David V. Nakles
Research Associate, Chemical Engineering
Carnegie-Mellon University

Michael J. Massey
ssistant Professor, Chemical Engineering/
ngineering & Public Policy
Carnegie-Mellon University

INTRODUCTION

ow and for the foreseeable future, pilot plant-scale effluent characterization data necessarily must serve as the only resource for vironmental assessment in high Btu coal asification processing. However, meaningful collection and interpretation of such data are complicated, since little if any effluent treatment is usually performed and large sections of these plants are typically nonscalable. In the absence of a data base and any established regulatory guidelines or standards, specification of an appropriate set of effluent characterization parameters is also complicated. The challenge in coal gasification environmental assessment is therefore two-fold:

1. to identify the set of effluent monitoring parameters, sampling/preservation/analytical procedures, and control characteristics appropriate to a comprehensive environmental characterization; and
2. to develop an effluent characterization strategy (both predictive and experimental) which properly addresses both the vagaries of measurements from small-scale plant operations and the sharp contrasts in effluent characteristics from process to process.

ERDA has assembled a combination of environmental contractors (see Figure 1) and a coordination contractor (Carnegie-Mellon University) to address these issues in an environmental assessment of its high BTU coal gasification pilot plant program. Details regarding the structure and operation of the program have been published elsewhere.(1,2) In the present paper, program methodology is discussed, available field data are presented, and preliminary trends in the effluent data base are explored in relation to evolving evidence of the fundamental relationship between process variables and effluent production.

BASIC STRUCTURE OF PROGRAM ENVIRONMENTAL ASSESSMENT PLANS

In the absence of any reference data base, assessment plans at each pilot plant are being formulated in two stages. Initially preliminary test plans have been developed to address basic issues of prioritization in stream and effluent parameter selection, alternative sampling methodologies, and validation of sample preservation and analysis techniques. Exploratory effluent characterization efforts have also been undertaken to identify significant effluent characteristics for later more comprehensive, quantitative investigations. Background analysis and preliminary test plans have been completed and documented for two pilot plants, Hygas and CO_2-Acceptor;(2,3) similar efforts are now in progress at the other participating plants.

Stream Sampling and Effluent Parameter Selections

Stream Sampling Selection

Plant streams are selected for sampling for one of three purposes (in decreasing order of importance): (1) to provide a baseline characterization of pilot plant effluent production *scalable* to larger plant sizes; (2) to provide material balances for specific effluent constituents; and (3) to determine pilot plant-specific environmental impacts. The critical issue of stream scalability is discussed below. First priority constituents for material balancing include sulfur, nitrogen, and trace metals. Stream characterization for pilot plant environmental impacts is receiving only minor attention in the program.

Pilot-scale versions of a process rarely reflect either the structural or the operational practices

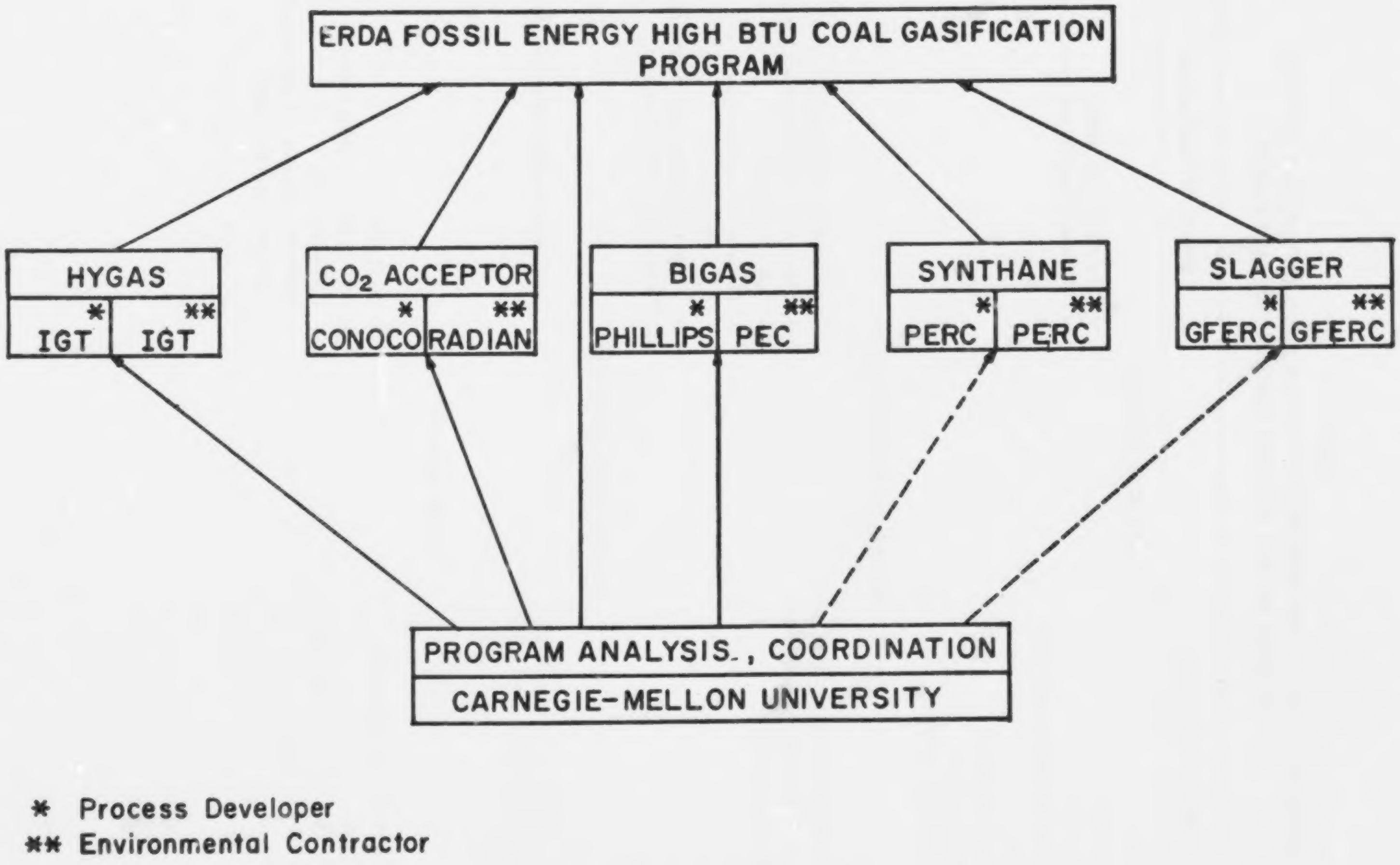
ERDA FOSSIL ENERGY HIGH BTU COAL GASIFICATION PROGRAM
HYGAS
* IGT
** IGT
CO_2 ACCEPTOR
* CONOCO
** RADIAN
BIGAS
* PHILLIPS
** PEC
SYNTHANE
* PERC
** PERC
SLAGGER
* GFERC
** GFERC
PROGRAM ANALYSIS., COORDINATION
CARNEGIE-MELLON UNIVERSITY
* Process Developer
** Environmental Contractor

Figure 1. Structure of ERDA Pilot Plant effluent characterization program.

TABLE 1

SUMMARY OF MAJOR ENVIRONMENTALLY SCALABLE AND NONSCALABLE SECTIONS OF PARTICIPATING HIGH BTU COAL GASIFICATION PILOT PLANTS

Scalable Plant Sections	Nonscalable Plant Sections
BI-GAS PILOT PLANT	
• Coal preparation • Coal slurry dryer • Raw product gas (prior to quenching) • Gasifier ash • High pressure gas washer • Water gas shift reactor • Selexol purification system	• Atmospheric vent washer • Wastewater handling and disposal system
CO_2-ACCEPTOR PILOT PLANT	
• Raw product gas (prior to quenching) • Regenerator offgas (prior to quenching) • Product gas quench system	• Regenerator offgas quench system • Regenerator offgas SO_2-scrubber system • Coal preparation • Coal venturi scrubber system • Regenerator ash • Wastewater handling and disposal system • Product gas purification system
GRAND FORKS PILOT PLANT	
• Raw product gas (prior to quenching) • Product gas quench sy[illegible] certain modifications)	• Wastewater handling and disposal system
HYGAS PILOT PLANT	
• Coal pretreater (tar, oil, wastewater, offgas streams) • Raw product gas (prior to quenching) • Product gas quench system • Gasifier ash	• Oil stripper • Product gas purification system • Coal preparation • Wastewater handling and disposal system • Coal venturi scrubber system

of subsequent commercial versions. In the specific case of existing coal gasification pilot plants, few if any plant effluent-bearing streams are processed as they would be in a larger commercial plant. As a result, conventional environmental sampling at the outfalls (air, water, land) of gasification pilot plants does not yield meaningful information. Instead, process stream sampling must be concentrated at points where effluent stream characterizations are scalable. Note that results of such sampling reflect process effluent production not emission levels, since sampling is undertaken upstream of any effluent treatment.

As shown in Table 1 the locations of scalable effluent streams vary widely among the four participating pilot plants in the environmental assessment program. With the exception of the Bi-Gas plant, coal preparation areas yield essentially no scalable effluent streams; virtually none of the plants have scalable wastewater handling and disposal systems; only the Bi-Gas plant operates a scalable product gas purification system; and only the Hygas plant operates a scalable coal pretreatment system. As a result, first priority scalable sampling efforts are concentrated on streams immediately linked to the primary gasification step, viz., raw product gases, gasifier quench condensates, and gasifier ash. Beyond these points, sampling efforts are tailored to the special scalable features of a given plant, e.g.,

- *Coal pretreatment* effluent data are being generated at the Hygas plant.
- *Product gas purification* performance data will be generated at the Bi-Gas plant.
- *Coal slurry dryer* performance data will be generated at the Bi-Gas plant.

Effluent Parameter Selection

Procedures for the identification, grouping, and ranking of effluent parameter priorities have been published elsewhere;(2,4) a summary of current priorities is provided here in Table 2. Essentially all of the parameters listed in Table 2 either have or will be surveyed during the course of initial plant screening efforts. The subset of parameters found to be significant in this screening will be retained in subsequent more comprehensive sampling and analysis efforts.

TABLE 2

SUMMARY OF FIRST PRIORITY EFFLUENT PARAMETERS IN THE ERDA ENVIRONMENTAL ASSESSMENT PROGRAM

Wastewater Effluent Parameters (2,4)

- pH
- TSS
- BOD_5
- COD
- Phenols
- TOC
- Grease and Oil
- F^-
- $S^=$
- CN^-
- $NH_3 - N$
- $NO_3^- - N$
- $PO_4^{\equiv}$

Trace Wastewater Effluent Parameters(2,4)

- Al
- As
- Cd
- Cr
- Cu
- Fe
- Hg
- Mn
- Ni
- Pb
- Sn
- Zn

Gaseous Effluent Parameters(2,5)

- Sulfur Species: SO_2, SO_3, COS, CS_2, H_2S
- Other Acid Gases: NO_x, HC1, HCN, HF
- Other Inorganic Constituents: NH_3
- Other Organic Constituents: nonmethane HC's, e.g., C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}, C_4H_8

Stream Sampling Strategy

Major types of stream sampling methodologies include grab, composite, and continuous sampling. Typically one or more of these methods are combined to yield a working sampling strategy. Selection of the appropriate sampling strategy requires some knowledge of the nature of systematic and random variations in stream composition as well as an understanding of the use to which sample data will be put. For purposes of screening characterization, although a stream may be highly variable in composition, the large coefficient of variation of a grab sample may be adequate, and would certainly be the lowest cost sampling strategy. By contrast, sampling for material balance purposes may require a particular combination of grab and composite sampling strategy which yields a relatively lower coefficient of variation.

Use of Time Series Sampling

The systematic variability of an effluent stream composition with time can be determined by time series study of the behavior of selected effluent parameters. As illustrated in Figure 2 for three Hygas wastewater streams, the nature and the degree of variability differs significantly from stream to stream. Much of this variability (or in certain cases, the lack of it) can often be explained in terms of factors unrelated to actual effluent production. For example, operating practice accounts for a significant fraction of the variability in Hygas pretreater condensate composition.(6) Appropriate normalization of the data can often filter out some of this variability. A certain fraction of stream variability may represent actual changes in effluent production, which in turn are related to basic changes in process operating conditions.

Naturally, a sampling methodology designed to identify process variable/effluent production relationships would differ from that designed for simple screening characterization. However, given adequate time series data, statistical procedures available and described elsewhere(7,8) are adequate in either case for the selection of an appropriate combination of grab and composite sampling.

Specialized Sampling Requirements

Note that a low measured effluent stream coefficient of variation does not necessarily imply stable effluent production. For example, the large inventory (~2,000 gallons) of recirculating quench water at Hygas and its dampening effect are responsible for the low observed variability of Hygas quench condensate. Determination and correlation of the actual variability of effluent production with time requires the sampling of raw product gases prior to quenching. C-MU has developed and described elsewhere(2) an apparatus for the sampling of such raw product gases. Preliminary shakedown tests were recently completed successfully. Exploratory time series sampling is scheduled to begin in October.

Validation of Sample Preservation and Analysis Procedures

Preliminary C-MU/IGT experimentation with Hygas wastewaters at the outset of the environmental assessment program pointed to the importance of prompt sample preservation and indicated potential problems with several traditionally recommended procedures for the preservation and analysis of coal and oil processing wastewaters.(9) Subsequent investigations by C-MU/Radian and C-MU/GFERC with CO_2-Acceptor and Grand Forks condensates, respectively, revealed additional evidence of analytical problems.(2) In particular, major analytical interferences of oils in the determination of thiocyanate were observed (Table 3) as well as the simultaneous degradation of cyanide and production of thiocyanate with time in unpreserved samples of gasifier quench condensate (Figure 3). Consequently, an ongo-

TABLE 3

CNS^- OIL INTERFERENCE(2)

Procedure	No. of Tests	CNS^- Spike, mg/1	Measured CNS^- Level, mg/1 Mean	Std. Dev.
Millipore	3	0	96.4	1.6
Filtration Only	3	50	151.8	2.1
Millipore	3	0	32.3	5.4
Filtration and Hexane Extraction	3	50	94.1	13.8

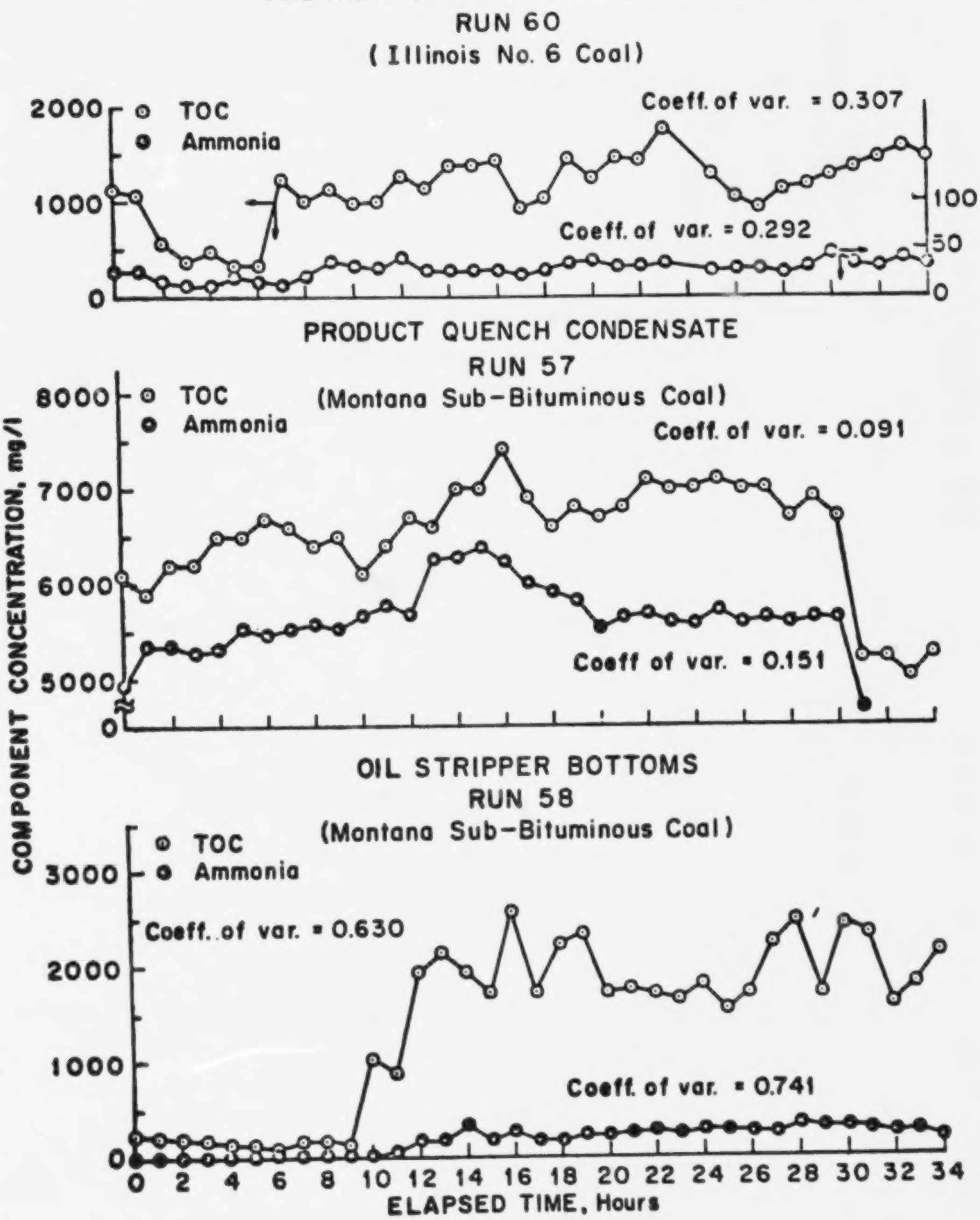

Figure 2. Time-series analysis: total organic carbon and ammonia contents of three major wastewater streams produced in the Hygas Pilot Plant.

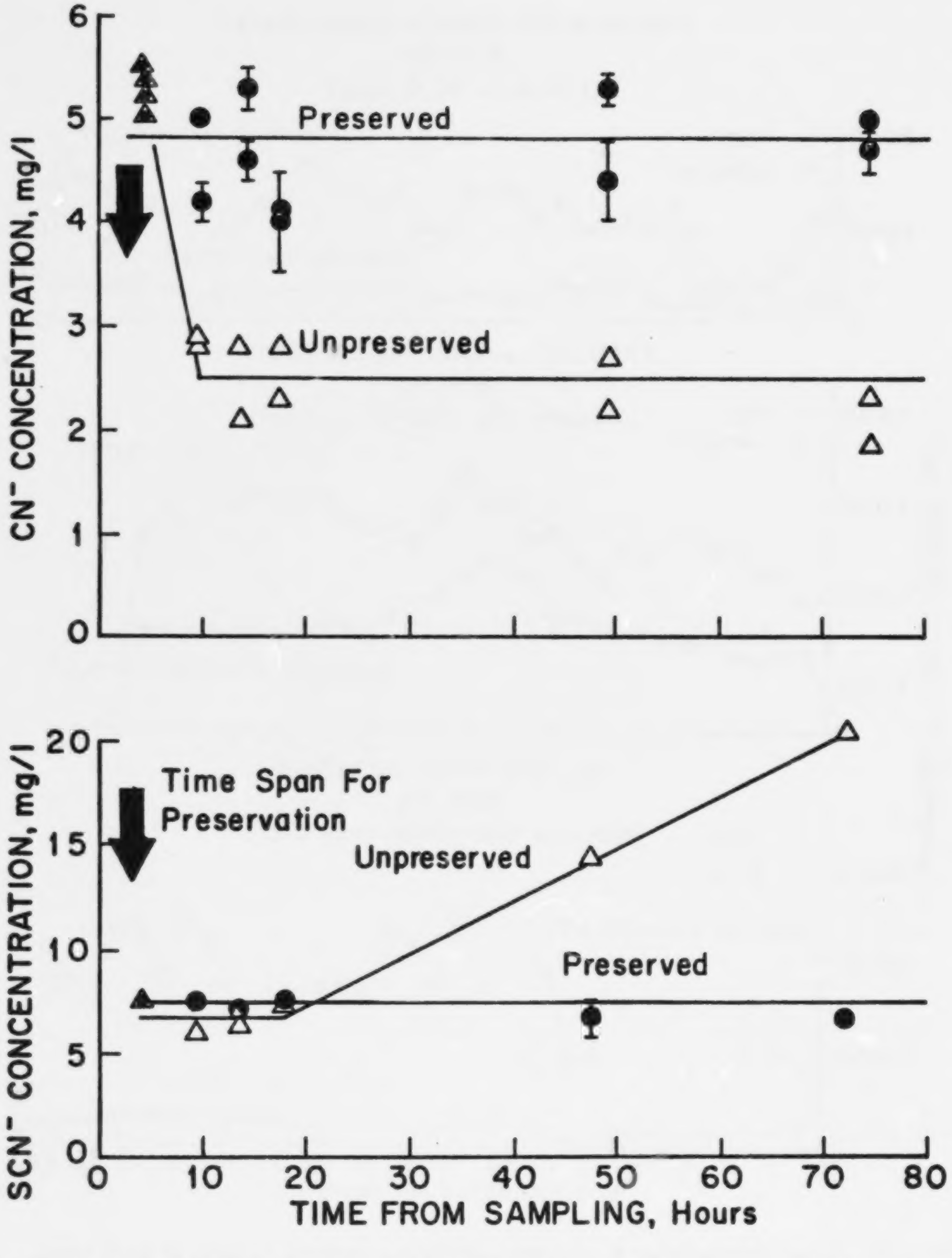

Figure 3. Time stability of cyanide and thiocyanate in preserved and unpreserved samples of gasifier quenchwater: Co_2-acceptor run 42.

ing effort of the program involves the investigation of the preservation techniques and analytical methods for the major liquid effluent parameters in coal gasification wastewaters. A set of recommended procedures for preservation and analysis has evolved from these initial investigations and is published elsewhere.(10) Research is also continuing on the complex relationships between cyanide and thiocyanate in these waters. Reaction mechanisms and kinetics for the conversion of cyanide to thiocyanate have been explored and the active sulfur species involved in the conversion has been investigated in both synthetic and actual gasification wastewaters. The results of these studies will be presented in the near future.(11)

SUMMARY OF AVAILABLE PROGRAM DATA

The major emphasis of the first year of the environmental assessment program has been on the characterization of the liquid effluents from the pilot plants. As noted, substantial work has been completed at the Hygas and CO_2-Acceptor pilot plants while initial efforts have just begun on the Bi-Gas, Synthane, and slagging fixed bed processes.

Characterization of Liquid Effluent Production

The initial characterization of the pilot plant liquid effluents, consistent with the overall program methodology, focused on those effluent streams which:

1. represent the bulk, by mass, of the total plant effluent production, and
2. have a direct and measureable linkage to the major process variables.

The liquid effluent streams in gasification which satisfy these criterion are the quench condensates of the gasification and/or pretreatment process steps. However, each pilot plant possesses liquid effluent flow patterns unique to its design and the determination of the total pilot plant effluent production may also involve other streams. The liquid flow patterns for the CO_2-Acceptor and Hygas pilot plants are shown in Figures 4 and 5, respectively, as are the major effluent streams which were sampled to yield the total liquid effluent production.

The total plant effluent production of these pilot plants for 10 major parameters (tars, oils, TSS, TOC, COD, Phenol, CN^-, CNS^-, NH_3, and $S^=$), normalized per pound of moisture and ash-free feed coal, is presented in Table 4. Also shown in Table 4 are the available normalized effluent production rates for the Lurgi-Westfield semi-plant and slagging fixed bed gasifier in Grand Forks. These normalized data are very amenable to analysis for the initial review of the effluent potential of the processes and the comparison and evaluation of these potentials among the existing plants.

Similarities and Differences in Pilot Plant Liquid Effluent Production Data

A cursory review of Table 4 reveals significant similarities and differences in the production of both organic and inorganic liquid effluents in the various pilot plants. For example, both the Lurgi and the slagging fixed bed plants exhibit quite similar tar production, ~60 to 80 lbs/ton coal, MAF; the Hygas and Lurgi processes produce similar quantities of phenol, ~11-12 lb/ton coal, MAF; the cyanide and sulfide production data for the Lurgi and CO_2-Acceptor plants are quite comparable, ranging from ~0.01 to 0.05 and 0.2 to 0.4 lb/ton coal, MAF respectively; and ammonia production is very similar for all the processes at ~15 lb/ton coal, MAF.

However, at the same time, there are also dramatic differences in the liquid effluent production data. In particular, tar, oil, and phenol production range from negligible to 80, 60, and ~15 lb/ton coal, MAF, respectively. Also, significant variations in cyanide, thiocyanate, and sulfide production are evident in Table 4, ranging from negligible to 0.04, 0.12 to 5.6, and 0.2 to 7.4 lbs/ton coal, MAF, respectively.

This large degree of variability is not surprising given the stage of development of the liquid effluent data base. Differences in coal feed type, sampling methodology, and sample preservation and analysis can possibly explain some of the variation, e.g., cyanide/thiocyanate interaction. However, some of the dramatic differences demonstrated by the hydrocarbon constituents, viz., tar, oil, and phenol, could not be accounted for in this man-

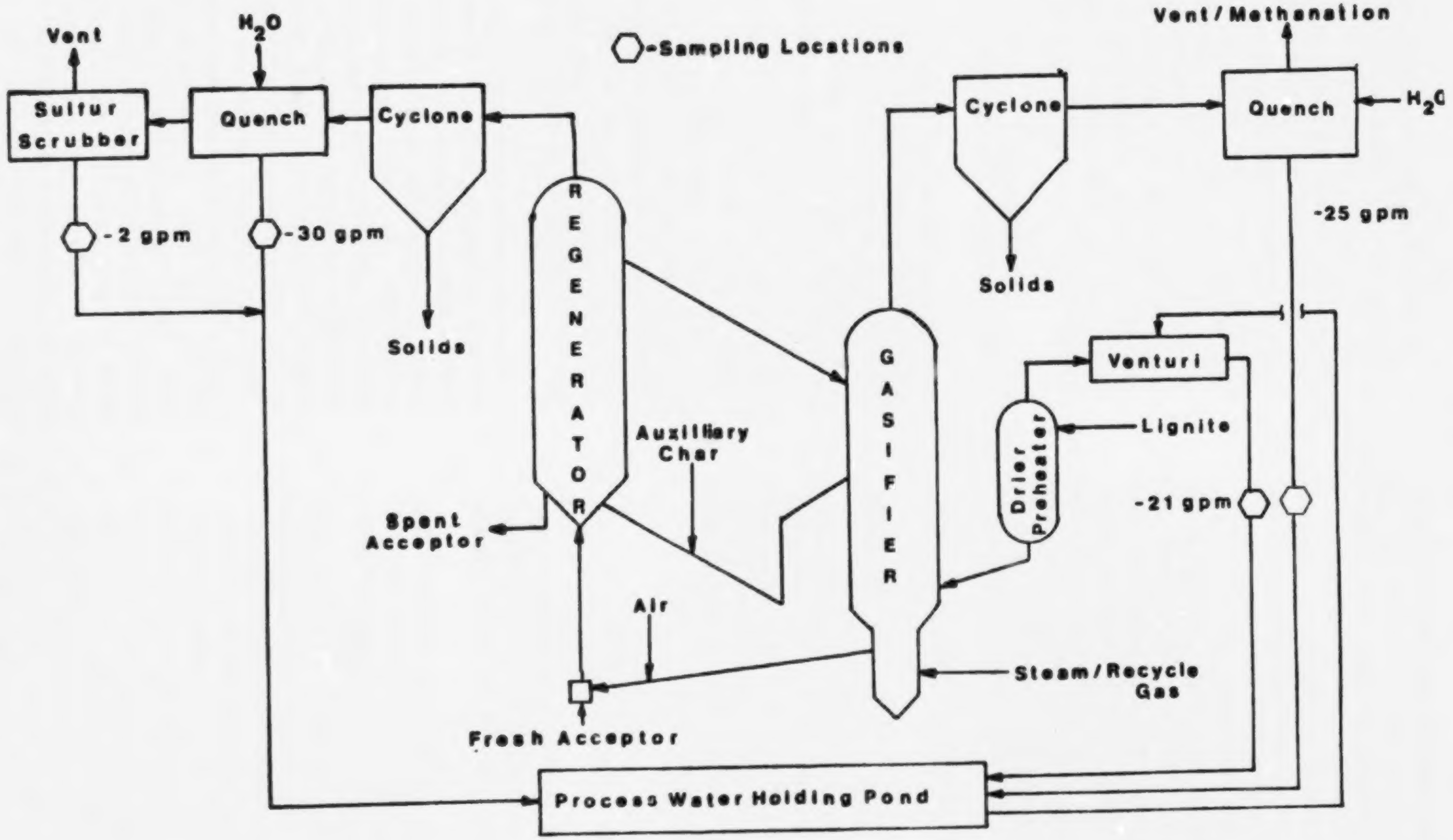
Vent
H_2O
Sulfur Scrubber
Quench
Cyclone
-Sampling Locations
Vent/Methanation
Cyclone
Quench
H_2O
-2 gpm
-30 gpm
Solids
REGENERATOR
-25 gpm
Solids
Venturi
GASIFIER
Auxiliary Char
Drier Preheater
Lignite
Spent Acceptor
-21 gpm
Air
Steam/Recycle Gas
Fresh Acceptor
Process Water Holding Pond

Figure 4. Liquid effluent flow patterns of the CO_2-acceptor coal gasification pilot plant.

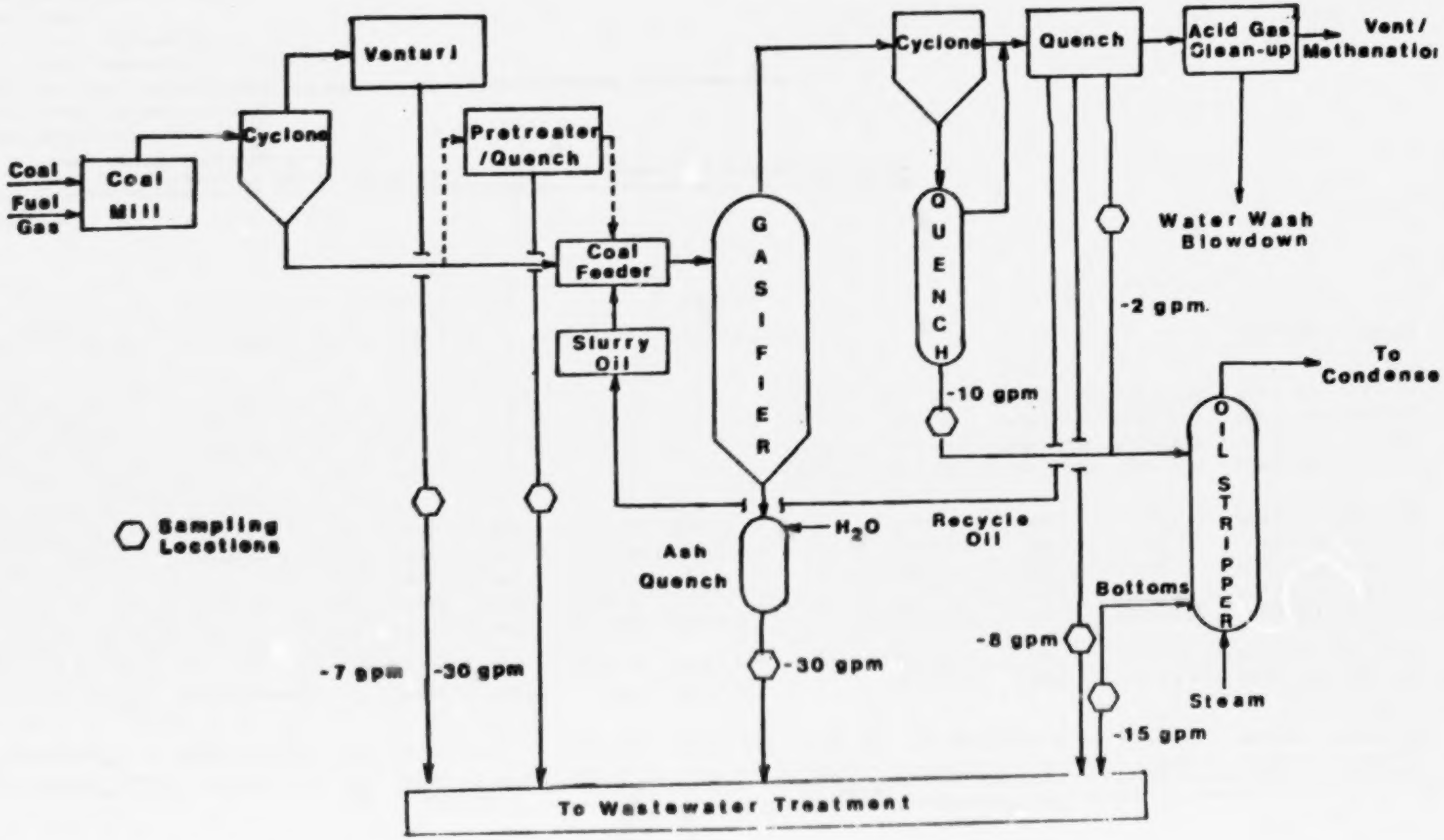
Coal
Fuel Gas
Coal Mill
Cyclone
Venturi
Pretreater /Quench
Coal Feeder
Slurry Oil
GASIFIER
Cyclone
QUENCH
Quench
Acid Gas Clean-up
Vent/ Methanatio
Water Wash Blowdown
-2 gpm.
-10 gpm
To Condense
OIL STRIPPER
Recycle Oil
H$_2$O
Ash Quench
Bottoms
-8 gpm
-15 gpm
Steam
-7 gpm
-30 gpm
-30 gpm
To Wastewater Treatment
Sampling Locations

Figure 5. Liquid effluent flow patterns of the Hygas coal gasification pilot plant.

TABLE 4

SUMMARY OF NORMALIZED LIQUID EFFLUENT PRODUCTION FROM OPERATING COAL GASIFICATION PILOT PLANTS

Process[a]	Coal Type	Run No.	Normalized Liquid Effluent Production, lbs/ton coal, MAF									
			Hydrocarbons		Aqueous							
			Tars	Oils	TSS	TOC	COD	Phenol	CN	CNS	NH_3	S
CO_2-Acceptor[b]	Glenharold Lignite	39	Negl.	Negl.	45 ± 26	0.45 ± 0.25	2.9 ± 0.75	0.05 ± 0.02	0.028 ± .005	0.12 ± 0.14	23 ± 15	0.39 ± 0.21
Hygas	Montana Lignite[c]	37	Negl.	Mod.[h]	-[g]	39.1 ± 15.4		11.4 ± 2.4	Negl.	2.5 ± 0.2	13.1 ± 0.3	0.2 ± 0.1
	Montana Sub-bituminous[d]	55	Negl.	Mod.	123 ± 59	40.0 ± 11.2	-	17.3 ± 2.8	Negl.	1.9 ± 0.6	27.7 ± 13.8	7.4 ± 0.2
		58	Negl.	Mod.	374 ± 112	10.9 ± 3.0	-	15.4 ± 3.5	Negl.	0.9 ± 0.2	14.8 ± 4.2	0.5 ± 0.2
	Illinois No. 6[d]	46	Negl.	Mod.	154 ± 96	5.7 ± 1.1	-	2.8 ± 1.5	Negl.	0.8 ± 0.3	17.1 ± 7.5	1.3 ± 0.7
		56	Negl.	Mod.	64 ± 42	7.0 ± 2.3	-	4.9 ± 0.9	Negl.	3.3 ± 1.9	12.9 ± 6.0	1.4 ± 0.6
		59	Negl.	Mod.	150 ± 90	30.2 ± 5.8	-	13.3 ± 4.1	Negl.	5.6 ± 1.5	3.4 ± 2.1	2.6 ± 1.6
		60	Negl.	Mod.	153 ± 122	25.2 ± 7.3	-	11.5 ± 3.9	Negl.	4.1 ± 2.5	14.9 ± 3.4	4.7 ± 2.0
Lurgi-Westfield[e] (Dry Ash)	Montana	-	61 ± 3	60 ± 5	-	-	56 ± 15	14.6 ± 3.0	0.01 ± 0.001	0.12 ± 0.14	11.9 ± 6.7	0.4 ± 0.2
	Illinois No. 6	-	62 ± 19	10 ± 4	-	-	32 ± 2	12.6 ± 1.6	0.04 ± 0.02	0.31 ± 0.08	16.8 ± 1.8	0.3 ± 0.1
	Illinois No. 5	-	78 ± 39	14 ± 5	-	-	44 ± 3	12.4 ± 0.1	0.02 ± 0.01	0.35 ± 0.06	16.4 ± 4.2	0.4 ± 0.2
	Pittsburgh No. 8	-	82 ± 4	18 ± 14	-	-	29 ± 1	7.9 ± 0.9	0.02 ± 0.02	0.34 ± 0.12	15.4 ± 0.7	0.2 ± 0.1
Slagging Fixed Bed (GFERC)[f]	N. D. Lignite	-	74 ± 1	-	-	15.4 ± 6.4	-	-	-	-	7.3 ± 0.2	3.6 ± 0.2
	N. D. Lignite	-	56 ± 7	-	-	8.4 ± 2.9	-	-	-	-	6.6 ± 0.8	-

Footnotes

(a) The Bi-Gas and Synthane pilot plants are presently undergoing start-up operation and are not included in this table. However, substantial effluent data have been generated on the Synthane pilot development unit and are reported elsewhere; References 12, 13.

(b) Source: Reference 14.

(c) Source: Reference 3.

(d) Total plant production derived from individual effluent streams presented in References 15 and 16.

(e) Source: Reference 17.

(f) Source: Reference 18.

(g) No data.

(h) Moderate production rates.

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ner. Such differences can only be explained by the inherent processing differences exemplified by each of the processes. The correlation of these process differences with the subsequent differences in effluent production is a complicated task. For example, why does the CO_2-Acceptor process simultaneously produce negligible quantities of tar, oil,[2] and phenol while the Hygas process, which also produces insignificant amounts of tar, yields significant amounts of oil and phenol? Or, why does the Lurgi process produce quantities of oil and phenol comparable to the Hygas process, yet produce much more tar? Understanding such phenomena requires the identification of the major gasification process variables which influence effluent production and subsequently, the specific relationships between these process variables and effluent production characteristics.

DEVELOPMENT OF PROCESS VARIABLE/EFFLUENT PRODUCTION RELATIONSHIPS FOR THE INTERPRETATION OF PROGRAM DATA

A combination of bench-scale, PDU-scale, and pilot scale experimental studies have been initiated to define the relationships between the process variables and liquid effluent production as an aid in interpreting the pilot plant effluent data bases.

Structure of Process Variable/Effluent Production Studies

Research initiated jointly by C-MU and the Pittsburgh Research Energy Center (PERC) in 1974 provides the framework for the comprehensive studies of the relationships between process variables and liquid effluent production.

Identification of Critical Process Variables

During a sequence of 19 controlled experiments on the Synthane pilot development unit, seven effluent production parameters (tar/oil, phenols, COD, TOC, TIC, CN^-, and CNS^-) were monitored both as a function of time and as a function of changing coal injection geometry (free fall, shallow, and deep bed-injection).(12,13) The typical response of the hydrocarbon effluents or indicators (tar/oil, phenols, TOC, COD) to the changes in feed geometry are demonstrated by the phenol production data shown in Figure 6. Note the dramatic reduction of phenol production as the coal was injected deeper into the fluidized bed. At the same time, significant changes in critical process variables also occurred as the point of fresh coal injection was altered from free fall to shallow and deep bed-injection:

1. Product gas residence time: Volatile materials evolved from the coal during its initial heatup were now forced to pass through the hotter, fluidized bed portion of the gasifier thereby increasing their residence time at conditions more conducive to attaining chemical equilibrium.
2. Gas-solid mixing: Coal injection now occurred in a region of intimate gas-solid contacting encouraging reaction of the volatilized species both with hydrogen and the highly reactive, potentially catalytic, char surfaces.
3. Mean reaction temperature: Longer residence times in the fluidized bed portion of the gasifier effectively increased the mean reaction temperature of the devolatilized coal species, and
4. Coal heat-up rate: Coal injection into the hotter fluidized bed effectively increased the heatup rate of the coal particles to their final temperature.

Table 5 summarizes the major impacts of changes in process variables on liquid effluent production demonstrated in that study. Examination of this table reveals that the largest percentage reduction in gasifier tar production, viz., 86 percent, resulted from the shift from free fall to shallow bed-injections of lignite. Accompanying this shift were major changes in coal heat-up rate, gas-solid mixing, and product gas residence time. However, increasing the depth of injection of lignite from 1-1/2 to 4-1/2 feet in the fluidized bed portion of the gasifier (deep bed-injections) and hence increasing the product gas residence time even more, resulted in an additional reduction of only 38 percent.

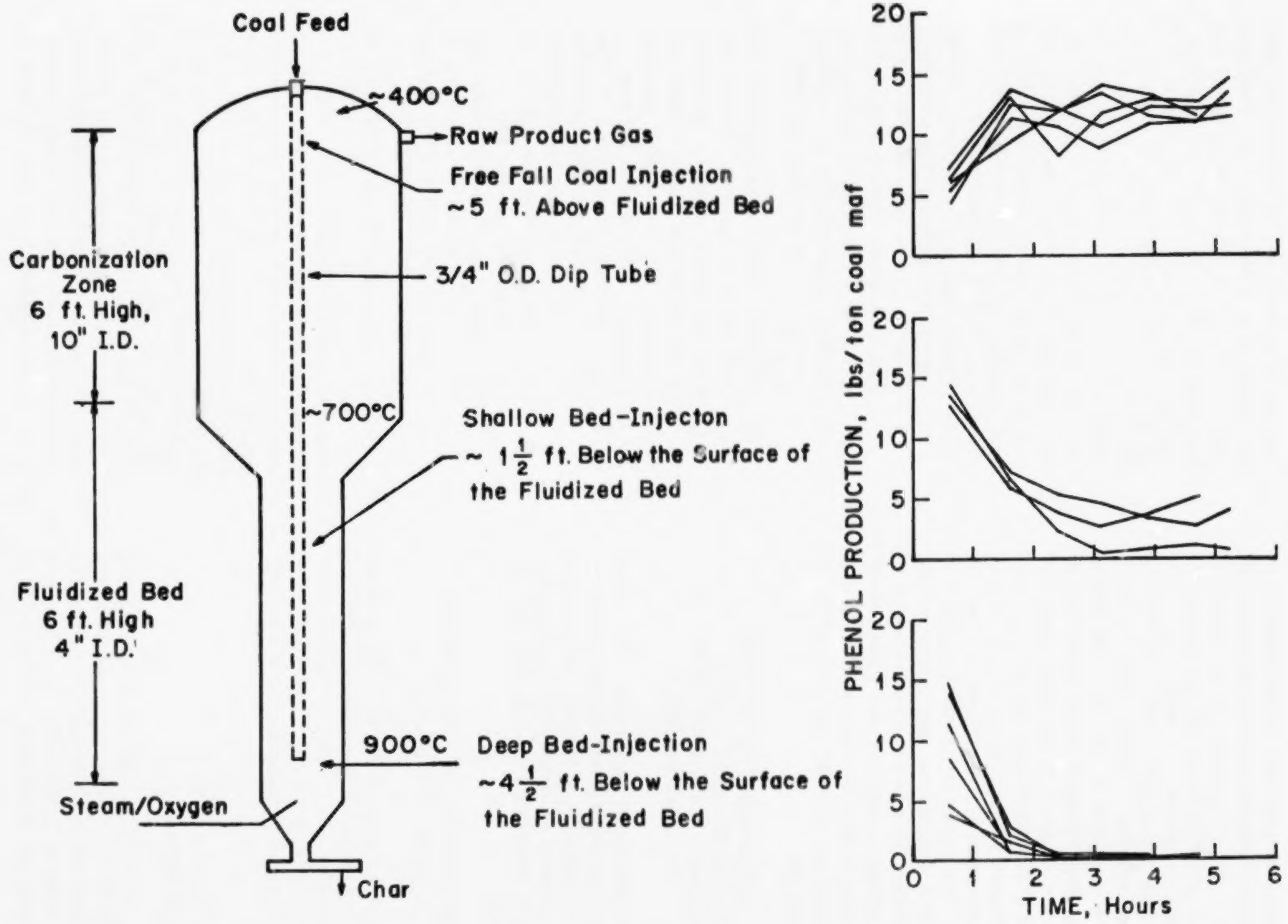

Coal Feed
~400°C
Raw Product Gas
Free Fall Coal Injection
~5 ft. Above Fluidized Bed
Carbonization Zone
6 ft. High,
10" I.D.
3/4" O.D. Dip Tube
~700°C
Shallow Bed-Injecton
~ 1 1/2 ft. Below the Surface of the Fluidized Bed
Fluidized Bed
6 ft. High
4" I.D.
900°C
Deep Bed-Injection
~4 1/2 ft. Below the Surface of the Fluidized Bed
Steam/Oxygen
Char
PHENOL PRODUCTION, lbs/ton coal maf
20
15
10
5
0
TIME, Hours
0
1
2
3
4
5
6

Figure 6. Influence of coal feed injection geometry on effluent production in the synthane pilot development unit.

TABLE 5

RELATIVE IMPACTS OF CHANGES IN MAJOR PROCESS VARIABLES ON SYNTHANE GASIFIER EFFLUENT PRODUCTION

		Decrease in Effluent Production			
Process Variables	**Nature of Increase**	**Tar/Oil**	**TOC**	**Phenol**	**COD**
	SHALLOW VS FREE FALL-INJECTION				
Reaction Temperature[(a)]	Major	86%	78%	71%	85%
Coal Heatup Rate	Major				
Residence Time[(b)]	Moderate				
Gas/Solid Contacting	Major				
	DEEP VS SHALLOW BED-INJECTION				
Reaction Temperature[(a)]	Minor	38%	44%	86%	69%
Coal Heatup Rate	Negligible				
Residence Time[(b)]	Major				
Gas/Solid Contacting	Negligible				

Notes:

(a) Mean reaction temperatures varied from 828° C (free fall) to 789° C (shallow bed) to 773° C (deep bed).

(b) Effective product gas residence time varied from zero (free fall) to 2.8 (shallow bed) to 6.6 seconds (deep bed).

Similar trends in chemical oxygen demand (COD) and total organic carbon (TOC) of aqueous effluents are apparent; COD's are reduced by 85 and 69 percent, TOC's by 78 and 44 percent, respectively. Interestingly, the above pattern does not hold for phenol production. Shifting from free fall to shallow bed-injections of lignite results in a 70 percent reduction in phenol production; however, increasing the product gas residence time by shifting from shallow to deep bed-injections of lignite results in a further reduction of 86 percent! Such evidence strongly suggests that different mechanisms may be responsible for observed reductions in various steady state effluent production rates with changes in fresh coal injection geometry.

Potential Mechanisms Governing Hydrocarbon Production

On the basis of the Synthane PDU test results, the following tenative mechanisms are proposed as major determinants in gasifier hydrocarbon formation and decomposition:

1. Phenols are inherently formed during the initial stages of coal heating and devolatilization, after which they are subject to decomposition by thermal cracking.
2. By contrast, tar/oil formation is strongly influenced by conditions and interactions during initial coal heat-up and devolatilization, e.g., gas-solid mixing, coal heat-up rate and hydrogen partial pressure. Formed material is then subject to decomposition by thermal cracking.

The first mechanism suggests that the determining factors in phenol production are reactor temperature and product gas residence time. The second mechanism suggests that net tar/oil production rates are the result of two contrasting process variable interactions: the first governs the extent of tar/oil formation and depends upon such variables as gas-solid contacting, hydrogen partial pressure, and coal heat-up rate; the second governs tar/oil decomposition and depends upon reactor temperature and product gas residence time.

Investigation of Hydrocarbon Formation/Decomposition Mechanisms: Experimenal Strategy

There are advantages and disadvantages to the study of the process variable/effluent production relationships at any single experimental scale. However, a judicious distribution of experiments across a range of scales affords an opportunity for maximum utilization of the advantages of each scale. Accordingly, as shown in Figure 7, a mixture of bench-scale, PDU-scale, and pilot scale experiments were designed to screen the major mechanisms influencing the formation/decomposition of hydrocarbons in coal gasification. In particular, information was sought to determine:

1. The susceptability of phenol to decomposition under gasification conditions, and
2. The relative impacts of formation phenomenon and thermal decomposition on the existence of tar/oils.

Studies of Phenol Formation-Decomposition

The postulated mechanism of intrinsic phenol production with subsequent decomposition by thermal cracking was examined on both the bench-scale and pilot plant scale.

1. Bench Scale Phenol Studies

The effect of reactor temperature and product gas residence time on the decomposition of phenolic compounds is amenable to examination using bench-scale apparatus operated under simulated gasifier conditions. C-MU and PERC recently completed initial experiments of this type on a model compound, phenol, and verified a thermal decomposition mechanism.(19)

The bench-scale experiments were conducted at atmospheric pressure in a homogeneous gas phase reactor (Figure 8) in which the reaction gas temperature, residence time, and composition were varied and the rate of phenol decomposition and the nature of the decomposition products were monitored. The range of conditions covered in these experiments included:

- Nominal reactor temperatures from 300 to 975° C, with primary emphasis on the range from 750 to 950° C,
- Nominal reaction gas residence times from 2 to 4 seconds, and
- Nominal hydrogen partial pressures of 0.0, 0.2, and 0.5 atmospheres, water partial pressure of approximately 0.5 atmospheres.

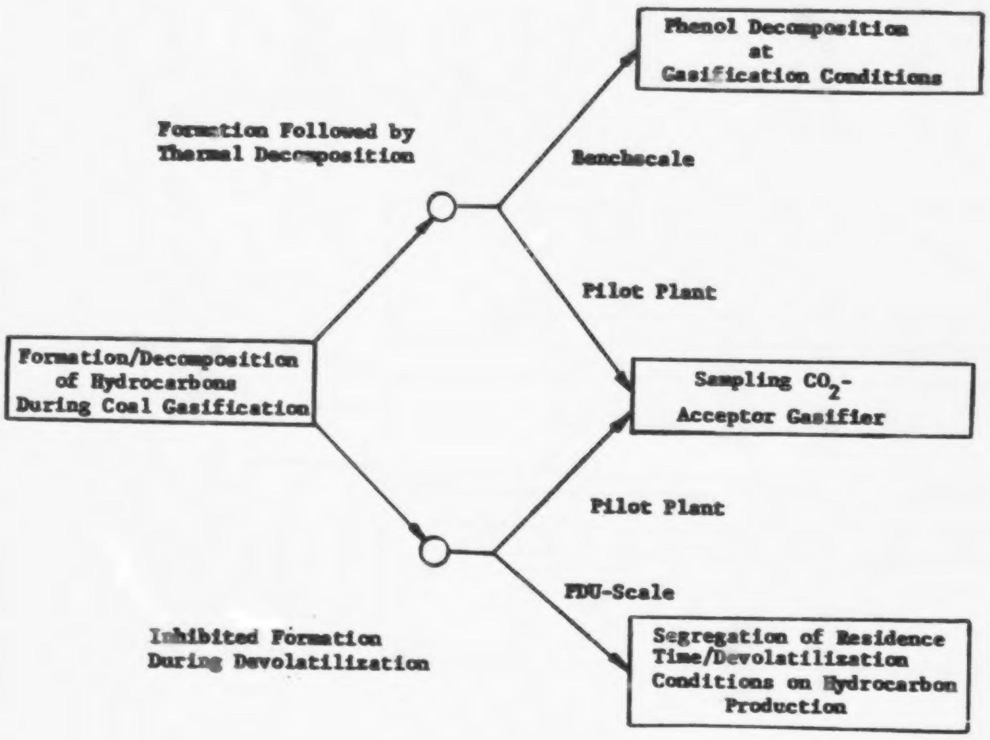
In addition to the homogeneous tests, two heterogeneous tests were also completed using gasifier char from the previous Synthane PDU tests. From this mixture of homogeneous and heterogeneous tests it was demonstrated that:

1. Phenol decomposition proceeds rapidly (2 to 4 seconds) by thermal cracking, at rates which are independent of reaction gas composition, particularly hydrogen partial pressure (Figure 9),
2. Phenol decomposition product distribution is a strong function of system hydrogen partial pressure, tar production increasing with decreasing partial pressure, and
3. The presence of solid surfaces reduces by at least 200° C (975 to 775° C) the reaction gas temperature required to accomplish rapid and essentially complete phenol decomposition (see Figure 9).

Future experiments are in progress to explore the decomposition kinetics of other prominant phenolic compounds (e.g., cresols) found in gasifier quench condensates. Additional atmospheric and possibly higher pressure experiments under heterogeneous reaction conditions will also be conducted.

2. Pilot Plant Phenol Studies

Very small amounts of phenol are produced in the CO_2-Acceptor process (Table 4). If phenol behaves as postulated, increasing phenol levels would be expected as process gas is sampled closer and closer to the coal injection point at the base of the gasifier. C-MU designed a sample probe to complete this experiment and it has been described in a previous document.(14) Preliminary sampling results have identified the presence of phenols at the point of coal injection in the CO_2-


Formation/Decomposition of Hydrocarbons During Coal Gasification
Formation Followed by Thermal Decomposition
Inhibited Formation During Devolatilization
Benchscale
Pilot Plant
Pilot Plant
PDU-Scale
Phenol Decomposition at Gasification Conditions
Sampling CO_2-Acceptor Gasifier
Segregation of Residence Time/Devolatilization Conditions on Hydrocarbon Production

- Phenol susceptible to thermal decomposition in homogeneous gas phase at 700 to 900°C and 2-4 seconds residence time
- 99% Decomposition observed at 970°C and a residence time of 2 to 4 seconds
- Char catalyzes decomposition of phenol: 99% decomposition at 750°C and a residence time of 2 to 4 seconds

- Preliminary results indicate the presence of phenol and other organics at the point of coal feed injection; however, quantitative analysis not yet available

- Heavy hydrocarbons (80% boil over 400°C) are very sensitive to gas/solid mixing and temperature at the point of devolatilization: 95% reduction by increasing both parameters on PDU gasifier
- Oil (boiling point 100-400°C) and phenol not influenced by gas-solid contacting and temperature at point of devolatilization

Figure 7. Preliminary screening of major mechanisms influencing the formation/decomposition of hydrocarbons in coal gasification.

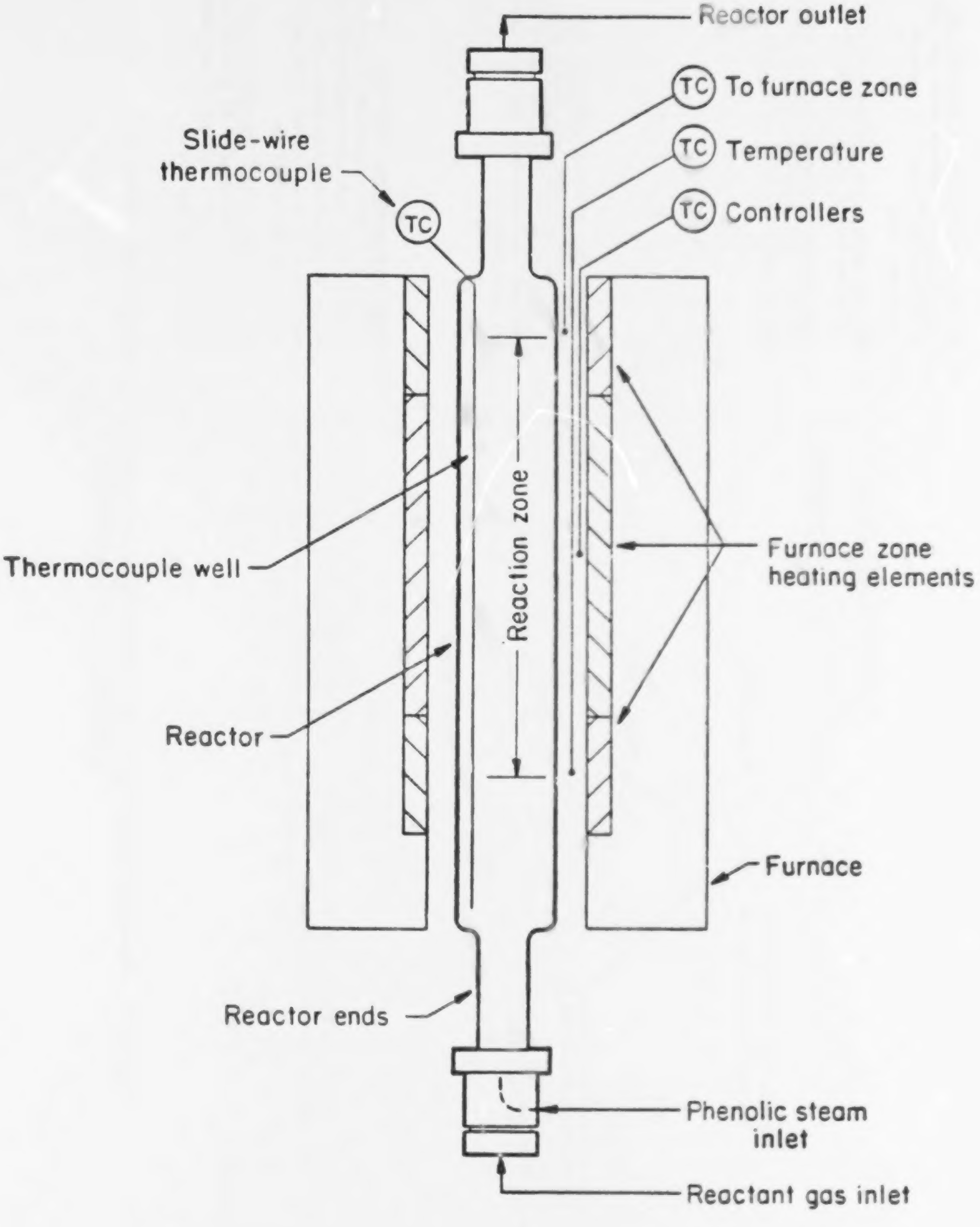

Reactor outlet
TC To furnace zone
TC Temperature
TC Controllers
Slide-wire thermocouple
TC
Reaction zone
Thermocouple well
Furnace zone heating elements
Reactor
Furnace
Reactor ends
Phenolic steam inlet
Reactant gas inlet

Figure 8. Thermal decomposition reactor and furnace configuration for phenol decomposition studies.

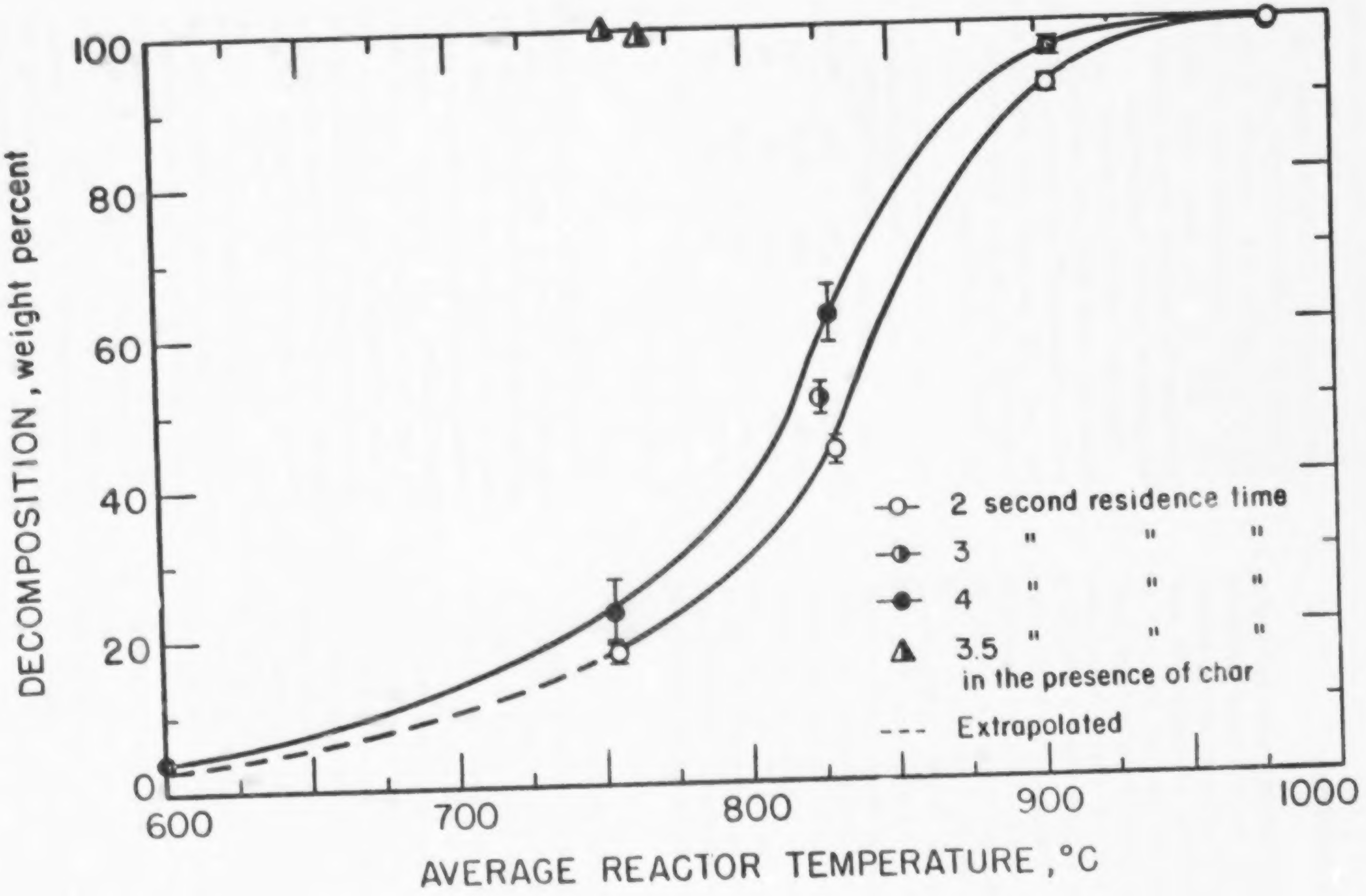


Figure 9. Measured phenol decomposition as a function of average reactor temperature for 2, 3, and 4 second nominal residence times.

Acceptor gasifier; however, further results are required before an extensive quantitative analysis can be done.

Studies of Tar/Oil Formation-Decomposition

It is believed that both formation and decomposition phenomena play an integral part in dictating the production of hydrocarbons produced during the thermal processing of coal. Bench-scale equipment are not adequate for the segregation of these formation/decomposition interactions since (1) the multicomponent nature of the tars and oils make it difficult to simulate these compounds for bench-scale decomposition studies and (2) studies based on simulated materials preclude the effects of process variables on the formation of tar/oils during devolatilization. Larger scale systems, operating on fresh coal and capable of examining both the effects of devolatilization conditions and thermal decomposition on tar yields, are required. This led to the initiation of two experimental programs - one on the Synthane PDU and the other on the CO-Acceptor pilot plant gasifier - to segregate the relative impacts of tar/oil formation and thermal decomposition on the existence of tar/oils under gasification conditions.

1. PDU-Scale Tar/Oil Studies

The use of a PDU-scale equipment train for the examination of process variable effects on tar/oil production and composition has some obvious advantages and disadvantages. While it provides a scale sufficient to preserve material balance capabilities and flexibility regarding changes of process conditions, it is very difficult to totally decouple individual process variables effects. However the purpose of the study was not to specifically isolate the effects of individual process variables; but rather, to dissociate the impact of tar/oil formation phenomenon and tar/oil decomposition on the existence of tar/oils. While the result of such a study may not yield quantitative mechanisms to explain the observed phenomenon, it should provide semi-quantitative empirical relationships which are quite amenable to scale-up and extrapolation.

The isolation of the decomposition and formation phenomenon in the Synthane PDU was accomplished by injecting the feed coal of the Synthane PDU gasifier directly onto the top of the fluidized bed (Figure 10). This provided devolatilization conditions similar to the shallow and deep bed-injection trials of the previous studies, e.g., gas-solid contacting, final reaction temperature, and coal heat-up rate, and at the same time essentially eliminated the residence time of the devolatilized species in the hot, fluidized bed.

Preliminary effluent production rates for these PDU trials have been summarized in a previous document(20) and are shown in Table 6 for tars (80 percent with boiling point >400° C), oils (boiling point between 100 and 400° C) and phenols:

Trial Description	Mean Particle Size (Micron)	Hydrocarbon Production (lbs/ton Coal, MAF)		
		Tars	Oils	Phenols
Free Fall-Injection	50	13±4 (6)[a]	48±10 (2)	8±2 (6)
Top Bed-Injection	50	0.6±0.3 (3)	49±38 (6)	9±6 (8)

[a] Number of Observations

These data are significant since they suggest that the tar reductions observed during the previous shallow and deep bed-injection trials were largely a result of the enhanced gas-solid contacting and temperature at the point of coal devolatilization. This statement results from the fact that a 95 percent reduction in heavy tar was accomplished with negligible product gas residence time in the fluidized bed (top bed-injection trials provide effectively no residence time for the product gas in the hot fluidized bed).

The mechanisms responsible for the tar reduction during coal devolatilization are not discernable from the PDU trials. However, enhanced gas-solid contacting and temperature during devolatilization have the potential to influence the secondary reactions of the devolatilized species. In particular, tar production could be reduced by (1) enhancing the reaction of the devolatilized species with

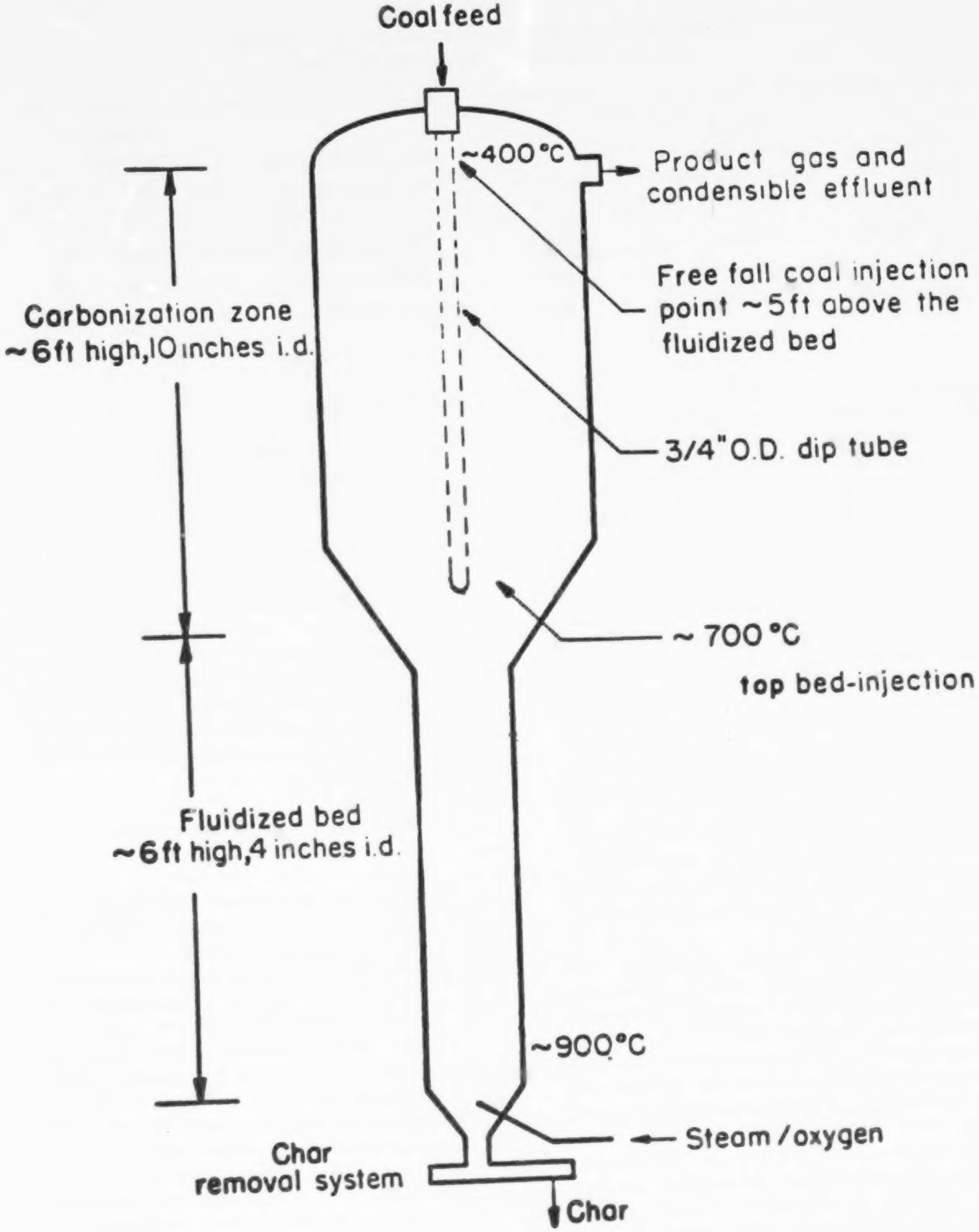

Coal feed
~400 °C
Product gas and condensible effluent
Free fall coal injection point ~5 ft above the fluidized bed
Carbonization zone ~6 ft high, 10 inches i.d.
3/4" O.D. dip tube
~ 700 °C
top bed-injection
Fluidized bed ~6 ft high, 4 inches i.d.
~900 °C
Steam / oxygen
Char removal system
Char

Figure 10. Synthane PDU gasifier: top bed-injection of feed coal.

TABLE 6

PROCESS VARIABLE AND EFFLUENT PRODUCTION PATTERNS FOR SELECTED COAL GASIFICATION PROCESSES

Process	Process Variable		Analogous Synthane PDU Coal Feed Geometry	Effluent Production		
	Gas-Solid Contacting During Devolatilization	Residence Time at Temperature		Tars	Oils	Phenol
Lurgi-Westfield	Minimal	Minimal	Free Fall-Injection	High	High	High
Hygas	Extensive	Minimal	Top Bed-Injection	Negl.	High	High
CO_2-Acceptor	Extensive	Extensive	Deep Bed-Injection	Negl.	Negl.	Negl.

hydrogen, thereby reducing repolymerization, or (2) providing additional surface area of the potentially catalytic char solids which may serve as sites for tar deposition/decomposition. Enhancing the stabilization of the devolatilized species by reaction with hydrogen would be expected to increase the quantity of lighter oils produced. Examination of the oil production reveals no such change (48 ± 10 versus 49 ± 38 for the 50 micron free fall and top bed-injection trials, respectively). Hence, deposition and/or decomposition of the tar species on the char surfaces may be the dominate mechanism of tar reduction. However, there is no data to verify or refute this hypothesis. Regardless of the mechanism, an empirical relationship has been identified between heavy tar production and gas-solid contacting during coal devolatilization at gasification temperatures (700° C). Thermal cracking or decomposition beyond this initial devolatilization point appears to contribute very little to the overall yield of heavy tar in gasification.

Not surprisingly, phenol production was statistically invariant (95 percent confidence level) for the change in injection geometries incorporated in this study. Both of the coal injection geometries used in the experiments provided no gas residence time in the fluidized bed and accordingly, phenol production for all the tests were aproximately equivalent. These data, combined with the previous bench-scale results, strongly support the original postulate that phenol is inherently formed during gasification and its destruction occurs via thermal decompositon.

2. Pilot-Scale Tar/Oil Studies

As with phenol, the CO_2-Acceptor pilot plant produces essentially no tar/oil effluent. Consequently, using the gasifier sample probe discussed earlier for sampling at the point of coal injection in the CO_2-Acceptor gasifier could also provide information concerning the relative impacts of formation and decomposition phenomenon on tar/oil existence. Preliminary data indicate the presence of some heavier hydrocarbons; however, the specific identification of these components has not yet been completed nor have their production rates been determined.

Preliminary Interpretation of Pilot Plant Liquid Effluent Data

Based on the bench-scale, PDU-scale, and pilot scale experimental studies completed at this time, it would appear that:

1. Phenol is indeed inherently formed during the heat-up and devolatilization of coal. Consequently, phenol production during gasification is directly related to the extent of thermal decomposition that occurs in the gasifier. This in turn, is influenced by residence time and temperature in the gasifier, and the presence of char solids, and
2. Heavy tar production, on the other hand, is dramatically influenced by devolatilization conditions, particularly

gas-solid contacting, and does not appear to be influenced by thermal decomposition phenomenon.

These semi-quantitative observations are quite useful in understanding the liquid effluent production of the various pilot plants presented earlier in Table 4 as well as providing the initial tools for the prediction of liquid effluent production levels for full scale commercial plants.

The relationships between process variables and liquid effluent production identified in the bench-scale and PDU-scale experiments are also demonstrated by the major gasification pilot plants. The free-fall, top bed-injection, and deep bed-injection coal feed geometries of the PDU effectively simulated the devolatilization conditions, i.e., gas-solid contacting and temperature, and product gas residence time conditions of the Lurgi, Hygas, and CO_2-Acceptor gasifiers, respectively. Accordingly, these pilot plants demonstrated qualitatively the same liquid effluent production characteristics as the equivalent feed geometries in the PDU (Table 6):

- Minimal gas-solid contacting/temperature and product gas residence time - high tar, oil, and phenol production,
- Extensive gas-solid contacting/temperature and minimal product gas residence time - low tar, high oil, and high phenol production, and
- Extensive gas-solid contacting/temperature and product gas residence time - low tar, oil, and phenol production.

The ability to correlate these process variables to liquid effluent production on the pilot plant scale represents a significant first step for the interpretation and prediction of liquid effluent production in full scale commercial facilities. In addition, this initial screening has indicated the direction for more detailed experimental work which will further define the critical relationships identified at this point. Perhaps more importantly, the methodology used to identify these process variable/effluent production relationships, that is, the process engineering approach to the collection of environmental data, may prove to be an invaluable tool necessary for the simultaneous development of new technologies and environmental regulatory policies in the United States.

FUTURE WORK

In the initial year of the ERDA coal gasification environmental assessment program, primary emphasis has been placed on activities which should lead to well-designed environmental test plans at each pilot facility. In field work at the pilot plants, this has led to an emphasis on wastewater studies, due to the lack of factual information concerning coal gasification wastewaters and the potential importance of such wastewater effluents. Although these studies are not yet completed, initial efforts have developed and verified wastewater sampling and analytical methods, and have produced a preliminary data base. Comprehensive environmenal assessment test plans for the ERDA pilot plants can now be based on the preliminary information obtained in these wastewater studies, as well as on information available from related and previous studies characterizing gas/liquid/solid waste streams from coal gasification.

With the completion of activities closely related to test plan formulation, emphasis in the next year can shift to the following priorities:

- Media emphasis will be refocused from wastewater studies to a balanced emphasis on all the media. In particular, characterization of gas streams and waste solid streams is seen as a priority. The characterization work includes efforts to measure the distribution and form of sulfur in coal gasification effluents, as well as efforts involving characterization of selected trace metals in effluent streams.
- Emphasis in planning activities will shift from environmental and process-related parameters (e.g., SO_2 in gas streams, COD in liquid effluents) tc those parameters useful fo characterization of potential occupational health problems in coal gasification (e.g., trace organics, hydrocarboı condensates). Efforts will be made t develop and verify basic methods fc characterization of these parameter

as well as carry out screening analyses in typical pilot plant streams.

- Data-gathering programs at the pilot plants are to emphasize the characterization of effluent streams which will have a counterpart in larger-scale facilities, for a range of important gaseous, wastewater, and waste solid components.

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TRACE ELEMENTS IN THE SOLVENT REFINED COAL PROCESS

By
R. H. Filby, K. R. Shah
Nuclear Radiation Center
Washington State University
Pullman, WA 99164
and
C. A. Sautter
Physics Department
Concordia College
Moorhead, MN

Abstract

Results are presented of a study of the distribution and fate of 34 trace elements in the Solvent Refined Coal Process Pilot Plant located at Fort Lewis, Washington and operated by the Pittsburg & Midway Coal Mining Co. under contract with the U.S. Energy Research and Development Administration. Neutron activation analysis was used to determine Ti, V, Ca, Mg, Al, Cl, Mn, As, Sb, Se, Hg, Br, Co, Ni, Cr, Fe, Na, Rb, Cs, K, Sc, Tb, Eu, Sm, Ce, La, Sr, Ba, Th, Hf, Ta, Ga, Zr, and Cu in feed coals, process solvent, Solvent Refined Coal (SRC-I) mineral residues, wet filter cake, sulfur, by-product solvents, process and effluent waters and by-product sulfur. A materials balance or budget was calculated for each element from the concentration data and the yields of each process fraction in the SRC process. The SRC-I and insoluble residue account for more than 90% of the input of each element, with other process fractions contributing little to the trace element balance. Except for Cl, Br, and Ti, each element was substantially lower in the SRC-I compared to the original feed coal. Two separate sets of samples were taken when the pilot plant had operated continuously for 7 days and composite samples were collected for each process fraction over a 24-hour period. The materials balance for each element (averaged for the two data sets) expressed as a percentage of the elemental input were: Ti (163), V (139), Ca (146), Mg (71), Al (97), Cl (84), Mn (136), As (106), Sb (127), Se (103), Hg (104), Br (159), Ni (133), Co (122), Cr (117), Fe (109), Na (127), Rb (119), K (100), Cs (97), Sc (120), Tb (112), Eu (100), Sm (108), Ce (110), La (108), Ba (108), Th (112), Hf (121), Ta (114), Ga (98), Zr (115), and Cu (132). The contents of all trace metals, including Hg, in plant effluent waters showed little variation from background level.

Coal liquefaction is a means of producing low sulfur, low ash fuels from coal which is a relatively dirty fuel for power generation compared to residual fuel oil. As the future energy needs of the United States are going to be met in large part by coal and coal-derived products in order to reduce dependence on petroleum, coal conversion will play an important role in the U.S. energy picture of the future. Both gasification and liquefaction processes are now under development and are at various stages of commercialization. Coal liquefaction is expected to provide chemical and refinery feedstock materials in addition to boiler fuels for energy generation, although this aspect of coal conversion is at present less attractive economically than the production of boiler fuels.

The Solvent Refined Coal Process (SRC-I process) developed by Pittsburg & Midway Coal Mining Company under contract with the U.S. Energy Research and Development Administration is presently at an advanced stage and a 50 ton/day Pilot Plant is operating at Fort Lewis, Washington. This pilot plant has undergone extensive testing and production runs of solid Solvent Refined Coal (SRC-I) have been made for power plant burning studies of the SRC-I product. The first successful commercial power generation from SRC-I was completed in the first half of 1977.

The widespread construction and use of coal conversion plants requires an evaluation of the environmental hazards associated with each process and plant. Among such hazards is the problem of potential emissions of toxic forms of some trace elements, for example As, Hg, Sb, or Se. An important objective of liquefaction processes is to remove much of the sulfur and mineral content of coal so that the resulting fuel can be burned without expensive stack scrubbers and meet stack emission specifications. It is thus important that the fate and distribution of trace elements in the SRC-I process be determined to assess the pollution potential of the fuel (SRC) and the environmental effects of emissions and effluent disposal. The distribution of trace elements present in the coal during liquefaction is also important in determining trace element materials balances in the process and to evaluate the effects of coal type, autocatalytic effects, temperature, pressure, solvent composition, degree of hydrogenation on the materials balance.

The objective of the study reported in this paper was to apply the technique of neutron activation analysis to the determination of trace elements in the SRC-I process. Neutron activation analysis was chosen as the method of trace element analysis because of the high sensitivity for many elements, good precision and accuracy, the multielement nature of the technique, and the capability of analyzing very different matrix types. This latter advantage is significant for the SRC-I project where very diverse materials are encountered, e.g. coal, SRC-I, filter aids, residues, process waters and volatile solvents.

Material balances have been measured for the elements Ti, V, Ca, Mg, Al, Cl, Mn, As, Sb, Se, Hg, Br, Co, Ni, Cr, Fe, Na, Rb, Cs, K, Sc, Tb, Eu, Sm, Ce, La, Sr, Ba, Th, Hf, Ta, Ga, Zr and Cu. A preliminary study was carried out when the SRC-I pilot plant was operating at non-steady state conditions and the data from this study have been reported previously[1,2]. Later two material sets were collected after the pilot plant had operated continuously for at least 7 days and these are referred to as equilibrium (or steady state) sets (1 and 2) and the trace element data obtained are discussed in this paper.

The Solvent Refined Coal (SRC-I) Process

A schematic diagram of the SRC-I process is shown in Figure 1. Coal is crushed, ground and dried, mixed with a solvent (recycled in the process) to form a slurry which is hydrogenated in a reactor at 455°C at 1500 psig. After the reactor, process gases (C_1 - C_4 hydrocarbons, CO_2, H_2S, CO, H_2, etc.) are flashed off and the liquid is filtered through pre-coated rotary drum filters to remove unreacted coal and mineral matter. Light oils and process solvent are flashed off the liquid to give a solid product, SRC-I, and the solvent recycled back into the system. In this process the coal is dissolved in the solvent and, depolymerized to give smaller molecules in the presence of hydrogen.

Much of the organic sulfur is converted to H_2S and some of the FeS_2 is converted to FeS + H_2S

i.e. $FeS_2 + H_2 \rightarrow FeS + H_2S$

$$R\text{-}S\text{-}R^1 + 2H_2 \rightarrow H_2S + R\text{-}H + R^1\text{-}H$$

Approximately daily rates of production of trace elements in the 50 ton/day pilot plant are shown in Table 1. The fate of trace elements present in the coal during the process is dependent on a) the nature of the element and b) the chemical bonding of the element in the coal matrix i.e. organically bound or inorganically present as mineral species. Under the reducing process conditions (high H_2 pressure, 455°C, 1500 psig) several elements may be volatile or form volatile species, e.g. Hg^0, H_2Se, AsH_3, SbH_3, HBr, $Fe(CO)_5$, and $Ni(CO)_4$, among others. Whether such species will be formed will depend largely on the nature of the host mineral (or maceral) and whether this mineral is reactive under the liquefaction/hydrogenation conditions. In addition to the volatile species that might escape in gaseous emissions or condense with distillate products, there is the possibility of reaction with the organic matrix to form organometallic compounds, many of which are extremely toxic and some of which are volatile. Many of the transition metals (e.g. Ti, Fe, Mn, Ni, Co, etc.) form a number of stable organometallic compounds with hydrocarbons or hydrocarbon-like molecules, for example the cyclopentadienyl compounds e.g. ferrocene $Fe(C_5H_5)_2$, titanocene Ti $(C_5H_5)_2$ and the many derivatives of the metallocenes, e.g. carbonyls, hydrides, salts, etc. Many of these are toxic and relatively volatile species and Table 2 lists some compounds that, if present, could be of environmental concern.

Unfortunately we have very little information on the fate of trace elements in coal during liquefaction, although it is obvious that the final molecular species of an element may be quite different from these encountered in coal because of the highly reactive conditions and

TABLE 1

PRODUCTION OF TRACE ELEMENTS IN 50 TON/DAY SRC-I PILOT PLANT

Minor Elements	Concentration in Coal (ppm)	Production Kg/day	Trace Elements	Concentration in Coal (ppm)	Production Kg/day
Fe	2.4%	1200	As	11.6	0.6
S	3.8%	1900	Sb	1.0	0.05
Al	1.1%	540	Hg	0.113	0.006
Ti	547	28	Se	2.2	0.1
Ca	630	32	Cl	286	15
Mg	860	44	Br	5.8	0.3
K	1260	64	Ni	18.0	0.9
Na	124	6.3	Co	5.3	0.3
			Cr	10	0.5
			Cu	22	1.1

TABLE 2

POSSIBLE ENVIRONMENTALLY IMPORTANT FORMS OF SOME TRACE ELEMENTS DURING LIQUEFACTION

Element	Volatile Species	Organic Species
As	AsH_3, $AsCl_3$, $AsBr_3$	$RAsH_2$, RR^1AsH R_3As, $R_4As^+X^-$
Sb	SbH_3, $SbCl_3$, $SbBr$, $SbOCl$	$RSbH_2$, RR^1SbH, R_3Sb
Hg	Hg metal, $HgBr_2$	R_2Hg, RHg^+X^-
Se	H_2Se, Se^o	$R\text{-}Se\text{-}R^1$; $R\text{-}SeO_3H$
Fe	$Fe(CO)_5$	$Fe(C_6H_5)_2(CO)_x$
Ni	$Ni(CO)_4$	Ni-asphaltene bonds
Ti	$TiCl_4$	$Ti(C_5H_5)_2$

the complex chemical system of the dissolution/hydrogenation process.

Trace Element Balances in Liquefaction

Very little information is available on the distribution of trace elements in coal conversion processes, although a number of preliminary studies have been made for gasification processes. Forney et al.[3] have studied the distribution of trace elements around the Synthane gasifier at PERC using mass spectroscopy. The results ranged from 218% recovery for F to 1103% for Pb and no reliable mass balances could be derived. Jahnig and Magee[4] presented some limited data on trace elements in SRC-I and related coals but no mass balances were calculated, nor were other process streams analyzed.

The work reported here is thus the first attempt at calculating trace element balances in the SRC-I process.

ANALYTICAL METHODS

Sample Collection and Preparation

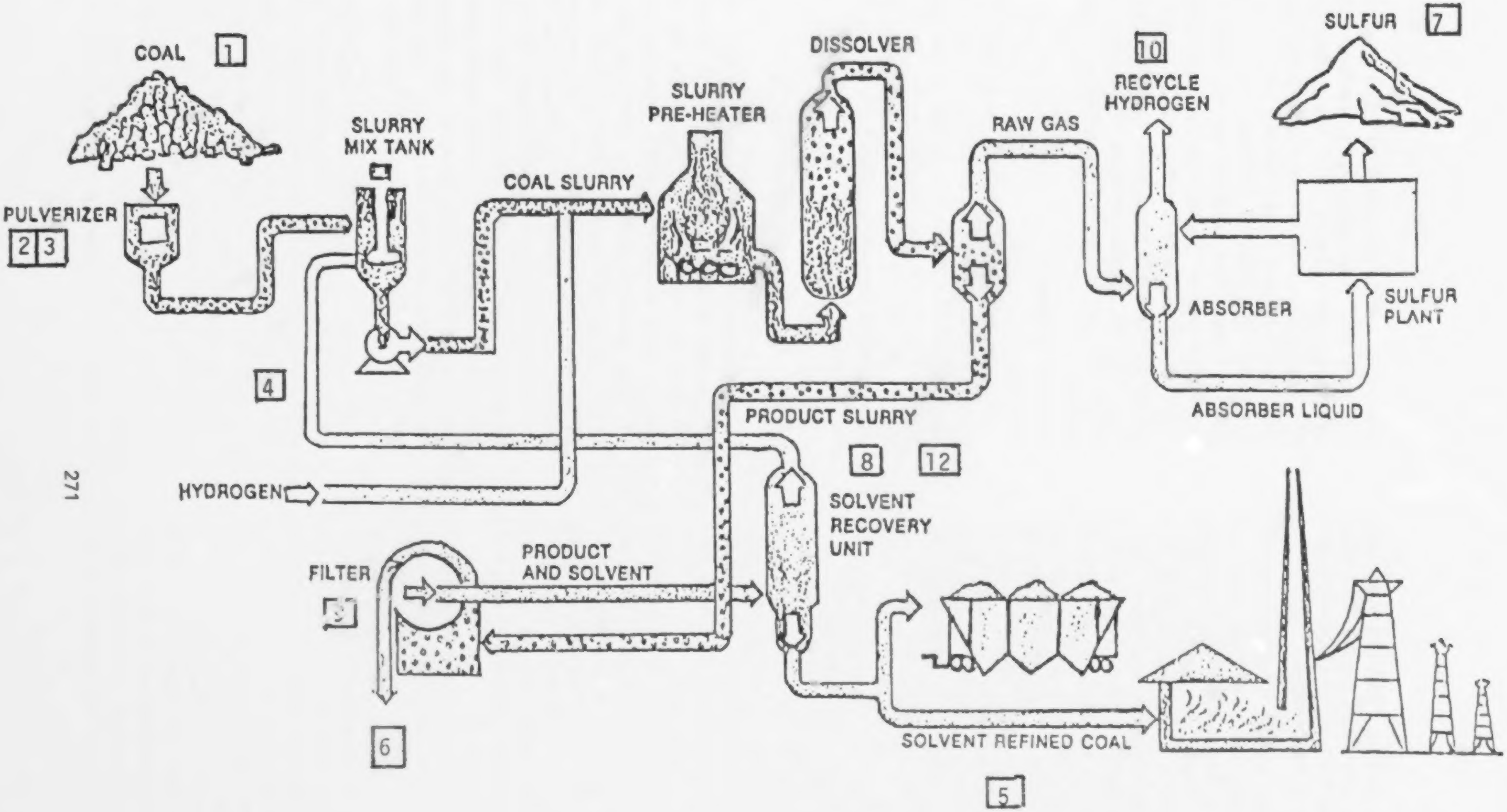
In order to evaluate the fate of elements in the coal liquefaction process, the sample collection procedure is critical. Samples collected should not only cover various important process parameters but also be representative of the process stream sampled. After discussions with pilot plant personnel, twelve different points in the pilot plant were selected as the sample collection points. These points and materials collected are listed in Table 3 and shown on Figure 1. These points effectively

TABLE 3

PILOT PLANT SAMPLE COLLECTION POINTS

Sampling Point	Description	Matrix	Amount
1.	Raw coal	solid	50 gm
2.	Dried/pulverized coal	solid	50 gm
3.	Dust collector	solid	10 gm
4.	Recycle solvent	organic solvent	1000 ml
5.	Solvent refined coal	solid	100 gm
6.	Mineral residue	solid	50 gm
7.	Elemental sulfur	solid	100 gm
8.	Light ends	organic solvent	2 quart
9.	Filter-aide	solid	50 gm
10.	Process water	aqueous	350 ml
11.	Treated effluent water	aqueous	350 ml
12.	Fresh Wash Solvent	organic solvent	1000 ml

SOLVENT REFINED COAL PROCESS


COAL
1
PULVERIZER
2
3
SLURRY MIX TANK
4
COAL SLURRY
SLURRY PRE-HEATER
DISSOLVER
RAW GAS
10
RECYCLE HYDROGEN
SULFUR
7
ABSORBER
SULFUR PLANT
ABSORBER LIQUID
PRODUCT SLURRY
8
12
HYDROGEN
SOLVENT RECOVERY UNIT
FILTER
9
PRODUCT AND SOLVENT
6
SOLVENT REFINED COAL
5

11 Numbers refer to sampling points in Table 3.

covered all input, output, and other important process streams. Laboratory prepared samples were also analyzed to check any contamination of plant products by the process.

A representative sample was essential for this study. All samples should be collected when the plant is operating under a 'steady state' condition. This is very hard to achieve and as a compromise it was decided that the plant should be operating at least seven days without interruption prior to the sample collection. In order to nullify any effect of momentary fluctuation of the process conditions, all samples were collected for a period of 24 hours (every 4 hours) from each collection point. Final composites of samples were prepared by mixing samples collected during the 24-hour collection period for each point. Run conditions for equilibrium sets 1 and 2 are shown in Tables 4 and 5.

Samples collected for elemental analysis were divided into three groups depending upon sample matrix. They were a) solid samples, e.g. SRC-I, coal, residues, etc. b) organic solvents, and c) aqueous samples. Each type of sample required different procedures for the sample preparation, storage, and analysis. These procedures were:

Solid Samples: Solid samples such as SRC-I, ground coal, pyridine insolubles, etc., were collected in cleaned glass or polyethylene containers. These containers were soaked in dilute nitric acid for about 4 hours and then cleaned with double distilled water prior to use. The procedure was necessary to remove any surface contamination.

Organic Solvents: Solvents were collected in pre-cleaned brown glass containers, cleaned as above.

Aqueous Samples: Collection and shipping of aqueous samples required special attention. It is known that many elements are readily adsorbed on the wall of containers (plastic or glass) from the aqueous phase. The rate of adsorption varies from element to element and is often an irreversible process. It was found that if the aqueous samples were frozen immediately after the collection and kept frozen until analysis, the elemental adsorption process was kept to a minimum. It was also necessary that aqueous samples be free of suspended matter. In order to avoid both problems a special sample collection and shipping procedure was developed. Immediately after the collection, aqueous process streams were filtered through clean Nucleopore 0.4 μm filter in a Teflon filter assembly. The filtered samples were then quickly frozen. The aqueous filtered samples were collected in cleaned polyethylene bottles(200 ml) and in four different Playtex thin-walled polyethylene bags (each containing approx. 50 ml). These samples were shipped frozen by air freight to Washington State University.

Neutron Activation Analysis

Neutron activation analysis was used to determine the total of 34 elements, Ti, V, Mg, Ca, S, Al, Cl, Mn, As, Br, Na, K, Sm, La, Ga, Cu, Sb, Se, Hg, Ni, Co, Cr, Fe, Rb, Cs, Sc, Tb, Eu, Ce, Sr, Ba, Th, Hf, Ta, and Zr in all samples. Details of the procedures have been described elsewhere[1,2].

RESULTS AND DISCUSSION

The elements Ti, V, Ca, Mg, Al, Cl, Mn, As, Sb, Se, Hg, Br, Ni, Co, Fe, Cr, Na, Rb, K, Cs, Sc, Tb, Sm, Ce, La, Sr, Ba, Th, Eu, Hf, Ta, Ga, Zr and Cu were determined in the samples from the two equilibrium sets and from the SRC-I process pilot plant. The concentrations obtained in the important process fractions are shown in Tables 6 and 7 for Equilibrium Set 1. Due to lack of space the concentration data for equilibrium set 2 are not included, neither are the error values associated with each determination. In most cases, however, the relative standard deviations of each value (counting statistics) are less than 10% and in many cases are less than 5%.

Several points should be made concerning the concentration data. The concentration of each element in SRC-I is much lower than in the feed coal, except for Br which is the only element to show an increase. The percentage reduction in the SRC-I relative to the ground feed coal for equilibrium sets 1 and 2 are shown in Table 8. Bromine shows an increase in both equilibrium sets and it is not clear where the source of Br lies. Another point of interest, pertinent to the question of materials balances,

TABLE 4

RUN CONDITIONS FOR EQUILIBRIUM SETS

CONDITION	SET 1	SET 2	
RAW COAL FEED	3422.	3488.	#/HR
WATER REMOVED FROM COAL	233.	219.	#/HR
NET DEHUMIDIFIED COAL FEED	3188.	3269.	#/HR
MOISTURE FREE COAL FEED	3129.	3241.	#/HR
SOLVENT FEED FROM AREA 04	4635.	4240.	#/HR
SLURRY RECYCLE FEED	0.	0.	#/HR
SLURRY FEED TO PREHEATER	7823.	7509.	#/HR
SOLV.& REC. SLURRY TO DEH. COAL RATIO	1.45	1.30	
PERCENT SLURRY RECYCLE	0.0	0.0	PCT.
RECYCLE/TOTAL FEED RATIO	0.00	0.00	
HYDROGEN-RICH GAS FEED	201.	164.	#/HR
GAS FEED PURITY-MOL. PCT. H2	97.6	98.7	
HYDROGEN FEED	164.	140.	#/HR
HYDROGEN FEED	30855.	26306.	SCFH
SLURRY PREHEATER INLET PRESSURE	1623.	1631.	PSIG
SLURRY PREHEATER OUTLET TEMPERATURE	742.	752.	DEGF
DISSOLVER A PRESSURE	1545.	1498.	PSIG
DATE	3/1/76	5/14/76	

TABLE 5

YIELD DATA FOR EQUILIBRIUM RUNS

	Yield % MFC	
Product	Equil. Set 1	Equil. Set 2
H2	-2.75	-1.92
N2	0.02	0.00
C1	2.54	1.91
CO	0.02	0.79
C2	1.00	0.76
CO2	1.38	1.65
C3	1.16	0.92
C4	0.54	0.48
H2S	1.65	1.92
LT. OIL	2.53	2.90
H2O	5.00	5.00
WSH SOLV	7.77	3.11
PROC SOL	-8.90	-6.93
SRC	69.48	71.13
ASH	11.88	12.31
UNREA. C	6.12	6.00
COAL	-100.03	-100.02
TOTAL	0.00	0.00

TABLE 6

CONCENTRATIONS OF SEVEN ELEMENTS IN SRC-I STREAMS

Element	GC	SRC	PI	WFC	LO	PRS	WS	S
Ti (ppm)	530.1	465.0	3350	1490	2.04	19.1	0.92	<90.0
V (ppm)	30.1	4.63	195.2	140.6	0.050	0.445	0.052	8.2
Ca (ppm)	330	72.8	6300	3015	<10	<10	<5	<600.0
Mg (ppm)	1160	89.0	4000	4345	<10	<10	<7	<300.0
Mn (ppm)	34.0	20.3	185.0	140.0	0.18	2.09	0.2	8.0
Al (%)	1.18	0.02	7.72	5.5	50 ppm	43.9ppm	11.6ppm	<6 ppm
Cl (ppm)	260.1	159.5	759.6	1641.0	16.9	127	92.2	<40.0

GC	Ground coal	PI	Pyridine insolubles
WFC	Wet filter cake	LO	Light oil
PRS	Process recycle solvent	WS	Wash solvent
		S	Sulfur

TABLE 7

EQUILIBRIUM SET 1, RAW MATERIALS & PRODUCTS

	GC	SRC	PI	WFC	LO	PRS	WS	S	PW	EW
As (ppm)	12.5	2.00	85.7	62.1	0.011	0.24	0.011	<2.0	0.006	<0.001
Sb (ppm)	0.76	0.06	7.21	5.35	<0.4*	8.2*	<0.4*	<0.1	0.66*	2.0*
Se (ppm)	2.0	0.12	16.5	11.3	51.6*	24.0*	14.4*	<1.5	0.16	0.0012
Hg (ppb)	113	39.6	508	346	18.5	1.45	10.5	<100	106	3.2
Br (ppm)	4.56	7.74	12.0	20.7	0.015	1.0	0.02	<3.0	15.6	31.8
Ni (ppm)	14.9	<3.0	142	82.4	<0.03	0.4	<0.03	<28.0	<0.004	0.013
Co (ppm)	5.88	0.22	40.7	26.5	< 3.0*	40.7*	1.43*	110	0.2*	0.41*
Cr (ppm)	13.7	1.64	106	69.2	37.3*	3590*	41.3*	<2.0	0.007	0.15
Fe (%)	2.11	0.03	16.8	11.7	2.90*	211*	11.2*	<0.1	0.30*	1.25**
Na (ppm)	137	4.23	1020	623	0.60	0.50	0.45	3120	0.70	8.3
Rb (ppm)	<4.0	<0.5	66.5	37.1	<0.01	0.02	<0.01	<9.0	0.78*	0.52*
Cs (ppm)	0.75	0.02	5.08	3.20	1.06*	<1.2*	0.91*	<0.2	0.04*	0.02*
K (ppm)	1550	4.72	11100	6660	<0.1	0.25	<0.1	179	0.2	1.26
Sc (ppm)	2.59	0.57	14.8	9.26	0.15*	32.8*	0.19*	<0.02	0.13*	0.01*
Tb (ppm)	0.39	0.045	2.06	1.34	<0.13*	3.75*	<0.13*	< 0.1	0.01*	0.01*
Eu (ppm)	0.26	0.055	1.48	0.96	<0.01	<0.01	<0.01	<0.01	0.01*	0.01*
Sm (ppm)	2.62	0.29	16.9	8.16	< 0.01	0.02	< 0.01	0.61	0.08*	<0.06*
Ce (ppm)	20.9	0.45	156.0	102	<0.004	<0.004	<0.003	<2.0	<0.2*	<0.2*
La (ppm)	7.55	0.13	59.8	35.2	<0.01	0.01	<0.01	1.80	0.27*	0.5*
Sr (ppm)	88.6	<6.0	456.0	453	<0.6	<0.2	0.74	<45.0	<0.01	<0.04
Ba (ppm)	53.0	5.75	347.0	185.0	<0.1	1.14	<0.07	<39.0	<0.02	<0.04
Th (ppm)	2.00	0.22	12.8	7.70	<0.001	0.012	<0.001	<0.2	0.05*	<0.01*
Hf (ppm)	0.51	0.084	3.30	2.20	<0.001	0.003	<0.001	<0.2	0.02*	<0.01*
Ta (ppm)	0.14	0.046	0.71	0.42	<0.4*	2.53*	<0.3*	<0.2	0.02*	0.01*
Ga (ppm)	3.56	1.79	19.4	11.3	<0.01	0.06	<0.01	<1.5	<1*	<4*
Zr (ppm)	62.9	16.0	500.0	246	0.07	0.71	<0.1	<61.0	0.02	0.04
Cu (ppm)	19.9	2.07	189	138	0.03	0.68	0.03	<1.0	<12*	<10*

Note *Values in ppb: **Values in ppm PW Process Water EW Treated Effluent Water

TABLE 8

TRACE ELEMENT REDUCTION SRC COMPARED TO COAL

Element	SRC/G.Coal	% Reduction	Element	SRC/G.Coal	% Reduction
Ti	0.88	12	Ti	0.74	16
V	0.15	85	V	0.47	53
Ca	0.22	78	Ca	0.22	78
Mg	0.08	92	Mg		
Al(%)	0.02	98	Al(%)	0.03	97
Cl	0.61	39	Cl	0.34	66
Mn	0.60	40	Mn	0.40	60
As	0.16	84	As	0.07	93
Sb	0.08	92	Sb	0.04	96
Se	0.06	94	Se	0.03	97
Hg	0.35	65	Hg	0.41	59
Br	1.70	+70	Br	1.33	+33
Ba	0.11	89	Ba		
Th	0.11	89	Th	0.10	90
Hf	0.16	84	Hf	0.12	88
Ta	0.39	61	Ta	0.29	71
Ga	0.50	50	Ga	0.19	81
Zr	0.25	75	Zr	0.08	92
Cu	0.10	90	Cu	0.08	92
Na	0.03	97	Na	0.04	96
Rb			Rb	0.02	98
Cs	0.03	97	Cs		
K	0.003	100	K	0.001	99.9
Ni			Ni		
Co	0.04	96	Co	0.05	95
Cr	0.12	88	Cr	0.37	63
Fe	0.01	99	Fe	0.01	99
Sc	0.22	78	Sc	0.15	85
Tb	0.12	88	Tb	0.09	91
Eu	0.21	79	Eu	0.14	86
Sm	0.11	89	Sm	0.07	93
Ce	0.02	98	Ce	0.02	98
La	0.02	98	La	0.01	99

is that only SRC and fractions derived from the mineral residues (i.e. mineral residue, pyridine insolubles) show significant concentrations of trace elements.

The high concentrations of Ti in the SRC-I are only slightly lower than in the original coal. In SRC-I from equilibrium set 1 the concentration is 465 (in set 2 it is 490 ppm) and this represents only a 12% reduction compared to coal (10% for set 2). It is not known why Ti behaves so differently from all other metals studied but possible explanations are:

a) Ti is present in coal as an extremely finely divided oxide (TiO_2) which passes through the rotary drum filters.
b) Ti is present as an organometallic species in coal, soluble in the process solvent.
c) Ti is present in an inorganic combination (i.e. mineral form) but reacts to form an oil-soluble compound ($TiCl_4$) or an organometallic species) during the hydrogenation reaction.

There is some evidence[5] that suggests the presence of an organometallic species in SRC-I, but the form of Ti in SRC-I is outside the scope of this paper.

Materials Balance Calculations

One of the main objectives of this study was to determine the fate of trace elements in the SRC-I process and to determine a materials balance for each element, particularly those known to be, or suspected of being toxic. To do this, it is necessary to know the elemental concentration of each process fraction and the weight yield (in % from original coal) of each fraction. The run data shown in Table 5 provides information on the yields of SRC-I, Light Oils (LO), Wash Solvent (WS), Process Water (PW), and Sulfur (from H_2S yields). However, it is difficult to assign a contribution to the recycle process solvent yields so that we have arbitrarily assigned a value of 5% for this fraction. In quantitative terms, the recycle process solvent contribution to the overall materials balances is negligible and the error associated with the assigned yield is small. A more difficult problem concerns the contribution of the filtered residue to the materials balance. Several residues were analyzed viz: pyridine insolubles (PI), mineral residue, wet filter cake (WFC) and ash of pyridine insolubles. We have chosen to base the "residue" component of the materials balance on the pyridine insolubles because a) the solvent-soluble material has been washed out compared to the filter cake, and b) no elements have been lost by ashing (very important for Hg, Se, and As) as compared to the ash of the pyridine insolubles. The pyridine insolubles thus represent inorganic mineral matter and any unreacted coal. However, we did not have run data on pyridine insolubles. Consequently we computed the PI contribution by assuming that 100% of K from the coal is in the PI and this appears reasonable considering the very low K content of SRC-I compared to the input coal. When computed in this way the PI yield per unit of coal is 13.9% for Run 1 and 18.1% for equilibrium set 2. The proportions of each fraction (coal = 1.0) for the two equilibrium sets are shown in Table 9. The material balance for each element in percent of input from coal are given in Table 10.

In these calculations we have assumed that the only contributions to the trace element input is the coal. This assumption naturally does not take into account contributions from the recycle process solvent (small), H_2 gas (small) or from corrosion and wear of the construction materials (possibly important for some elements). For equilibrium set 2 the balances range from a low value of 82.3% (Cl) to a high of 293% for Ca. Except for Ca, Ni, Ti, V, and Cr all balances lie within the range 83 - 145% which may be regarded as excellent given the assumptions made and the errors associated with obtaining representative samples of the process streams. For equilibrium set 1 the values range from 53% (Mg) to 259% (Rb). Except for Mg (53%), Rb (259%) and Br (172%) all values lie within the range 85 - 150% which may be considered excellent.

Of particular significance are the materials balances for Hg, As, Se, Sb and Br. For Hg, a volatile element, the materials balances are 98% and 109% for sets 1 and 2 and this shows that all the Hg in the process is accounted for. It should be noted that the recycle process water of equilibrium set 1 accounts for 10% of the total. Mercury is the only element

TABLE 9

PROCESS FRACTION CONTRIBUTIONS TO MATERIALS BALANCES

Process Fraction	Contribution Equilibrium Set 1	Contribution Equilibrium Set 2
Coal	1.00	1.00
SRC	0.695	0.711
PI	0.139	0.187
PRS	0.05	0.05
LO	0.023	0.03
WS	0.05	0.05
RPW	0.05	0.05
S	0.016	0.016
TOTAL	1.02	1.09

for which the RPW accounts for more than 1% of the total. Arsenic, antimony and selenium in equilibrium set 1 all balance well. For set 2 the very high As value is accounted for by an anomalously high concentration of As in the PI. This is being investigated. For Sb, and Se the balance is again good. For both sets, Br is high and there may be an external source of Br (probably solvents). Titanium is also high, 149% and 176% for sets 1 and 2 respectively. This may be due to corrosion of equipment or some other source. The high values for set 2 for Cr, Ni, and B may be due also to equipment corrosion. These three elements balance normally for equilibrium set 1.

Aqueous Environmental Samples

Several aqueous samples were analyzed in this study to determine the buildup of trace elements in the process water, treated effluent water and Hamer Marsh water (into which the plant effluent drains). Although there are significant concentrations of Hg, Se, As, and Cu in both process waters, these elements had been reduced to very low levels in the treated effluent water and in Hamer Marsh water. The efficient removal of these elements in the biotreatment plant appears to be primarily responsible for the low elemental concentrations in the plant effluent. High values of Se (6.3 ppm) and Hg (8.7 ppm) are found in the bio-sludge of equilibrium set 2 indicating the efficient removal of Hg and Se. Table 11 shows the concentrations of some important elements in samples from equilibrium set 2 because the set 1 samples did not include the biosludge. The analytical data for aqueous samples from set 1 are similar to those of set 2.

ACKNOWLEDGMENTS

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TABLE 10

MATERIALS BALANCES FOR EQUILIBRIUM SETS

Element	Set 1(%)	Set 2(%)	Element	Set 1(%)	Set 2(%)
Ti	149	176	Na	142	112
V	101	177	Rb	259	119
Ca	146	293	Cs	97	98
Mg	53	88	K	100	100
Al	92	102	Sc	95	145
Cl	85	82	Tb	81	143
Mn	129	143	Eu	94	105
As	106	-	Sm	97	119
Sb	137	118	Ce	105	115
Se	119	88	La	112	104
Hg	98	109	Ba	99	118
Br	172	145	Th	97	127
Ni	133	248	Hf	101	141
Co	129	115	Ta	94	135
Cr	117	272	Ga	110	86
Fe	112	105	Zr	128	102
			Cu	140	123

TABLE 11

SRC PILOT PLANT, AQUEOUS SAMPLES, EQUI. SET 2

	Process Treated Water	Effluent Water	Hamer Marsh Water	Bio-Sludge*
As (ppb)	10.7	<1.0	<5.0	<12.0
Sb (ppb)	1.0	0.64	0.5	1.21
Se (ppb)	914.3	0.37	0.45	6.28
Hg (ppb)	20.7	5.5	0.38	8.75
Br (ppb)	18.3		28.1	8.57
Ni (ppb)	14.0	16.0	7.0	12.0
Co (ppb)	0.43	0.36	0.26	4.48
Cr (ppb)	11.30	10.1	6.2	47.33
Fe (ppm)	1.34	0.41	0.36	12,000
Na (ppm)	5.1	8.0	42.4	9630
Rb (ppb)	0.77	1.36	0.91	2.66
Cs (ppb)	0.04	0.06	0.05	0.19
K (ppm)	0.73	<.10	<8	<200.0

*Note: All concentrations in the BioSludge are in ppm, not ppb

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ANALYTICAL TECHNIQUES AND ANALYSIS OF COAL TARS, WATERS, AND GASES

by

C. M. Sparacino,* R. A. Zweidinger,
and S. Willis

Chemistry and Life Sciences Divison
Research Triangle Institute
P.O. Box 12194
Research Triangle Park,
North Carolina 27709

Abstract

Analytical techniques applicable to coal gasification waste products (tars, waters, and gases) are described. Methodology for the qualitative analysis of these samples involves solvent partition, hplc, and gc-ms.

INTRODUCTION

One of the problems inherent in the investigation of a fuel conversion process such as coal gasification, is the development of analytical methodology that will permit an adequate assessment of the potential pollutants from such a process. In the case of laboratory scale gasifiers, this methodology can also be applied as a means of studying the effects of different coals and/or parametric variations on gasification. The need therefore is to develop a scheme which is reproducible, reasonably fast, and which can be applied to both volatile and nonvolatile pollutants (for gasification, those materials collected in tar and water traps located immediately after the reactor are considered nonvolatile, while those materials carried downstream with the gas are considered volatile).

Our appproach utilizes mass spectrometry as a basic means of identification. For volatile materials, components are collected directly from the gas stream onto polymer sorbents from which they are solvent extracted or thermally desorbed and transferred to a gas chromatograph-mass spectrometer-computer (gc-ms-comp). Nonvolatiles are subjected to a solvent partitioning process to separate the mixture into chemically similar groups. Each group is then either analyzed directly by mass spectrometry (ms) or is chromatographed using high performance liquid chromatographic (hplc) techniques and then subjected to ms analysis.

VOLATILES-QUALITATIVE ANALYSIS

Methodology pertinent to the collection and analysis of organic volatiles has been developed in our laboratories in relation to air pollution studies, and has been described in detail elsewhere.[1] By this process, the volatile organics are collected from the gas stream directly by passage of a portion of the stream through a glass cartridge containing Tenax GC (poly-*p*-2,6-diphenyleneoxide). The adsorbed materials are then removed *in toto* from the Tenax by thermal desorption and helium purge to a cooled (liquid nitrogen) capillary trap (Figure 1). The vapors are then released from the trap by rapid heating to 175°C, and transferred onto a high resolution capillary gc column. This column is interfaced to a double focusing mass spectrometer. Upon initiation of a run, the mass spectrometer continuously scans the column effluent from 28-400 amu approximately every 7 sec. The information from all scans is then accumulated by an online computer onto magnetic tapes. The data acquired includes peak intensities, total ion current (TIC) values and Hall probe signals (instrument calibration indicators). Up to approximately 1,000 spectra can be stored during a single analysis.

Processing the mass spectrometric data involves extraction of the TIC data and plotting TIC against the spectrum number. This yields a chromatogram which will generally indicate whether the run is suitable for further processing since it will give some idea of the number of unknowns in the sample and the resolution obtained using the particular gc column conditions. The computer is then directed to generate mass spectral plots of compound(s) represented by individual peaks in the TIC plot. Mass spectral plots consist of a plot of mass *vs* ion intensity and represent the characteristic mass spectra of the component(s).

Identification of resolved components can be

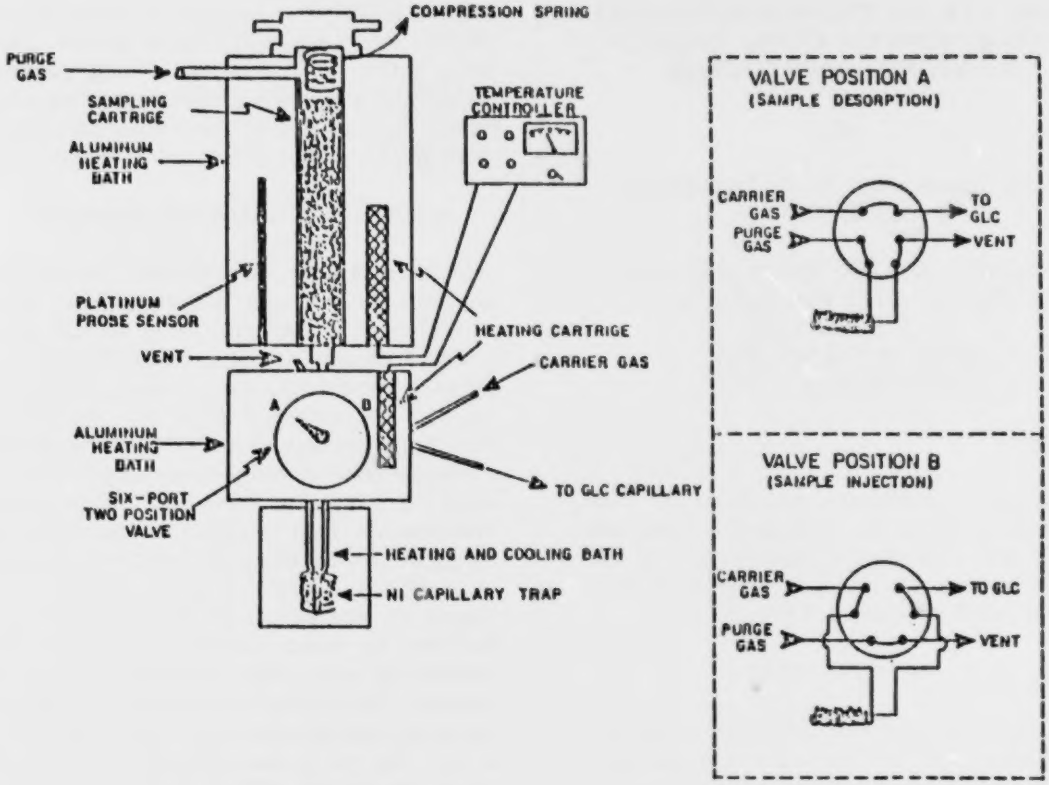
COMPRESSION SPRING
PURGE GAS
SAMPLING CARTRIGE
ALUMINUM HEATING BATH
TEMPERATURE CONTROLLER
PLATINUM PROBE SENSOR
HEATING CARTRIGE
VENT
CARRIER GAS
A
B
ALUMINUM HEATING BATH
SIX-PORT TWO POSITION VALVE
TO GLC CAPILLARY
HEATING AND COOLING BATH
NI CAPILLARY TRAP
VALVE POSITION A
(SAMPLE DESORPTION)
CARRIER GAS
PURGE GAS
TO GLC
VENT
VALVE POSITION B
(SAMPLE INJECTION)
CARRIER GAS
PURGE GAS
TO GLC
VENT

Figure 1. Thermal desorption inlet-manifold.

achieved by comparing the mass cracking patterns of the unknown mass spectra to an eight major peak index of mass spectra.[2] Individual difficult unknowns can be searched by use of various computerized systems such as Cornell University's PMB or STIRS systems, or the EPA MSSS. When feasible, the identification can be confirmed by comparing the unknown cracking pattern and elution temperature on two different gc columns with authentic compounds.

The treatment of volatile organics in the manner discussed has been applied not only to air samples, for which the process was developed, but to *in situ* coal gasification effluents. For the latter, some 200 neutral components have been identified. The method is reasonably sensitive: successful identification can be achieved with ~200 ng of individual component transferred onto the capillary column.

NONVOLATILES-QUALITATIVE ANALYSIS

The nonvolatile organics comprise those materials associated with the condensed tars and waters as isolated by in-line traps. These substances are exceedingly complex[3] and require fractionation before direct analysis can be undertaken. Other investigators have utilized either of two procedures for this process, column chromatography or solvent partition. Chromatographic methods separate the crude material into fractions of like polarity and can function as a useful means of reducing a complex sample into one or more manageable proportions.[4] Solvent partition schemes have been devised, most notably by researchers from the tobacco industry[5], in which group separations are accomplished on the basis of similar chemical properties, e.g., acids, bases, etc.

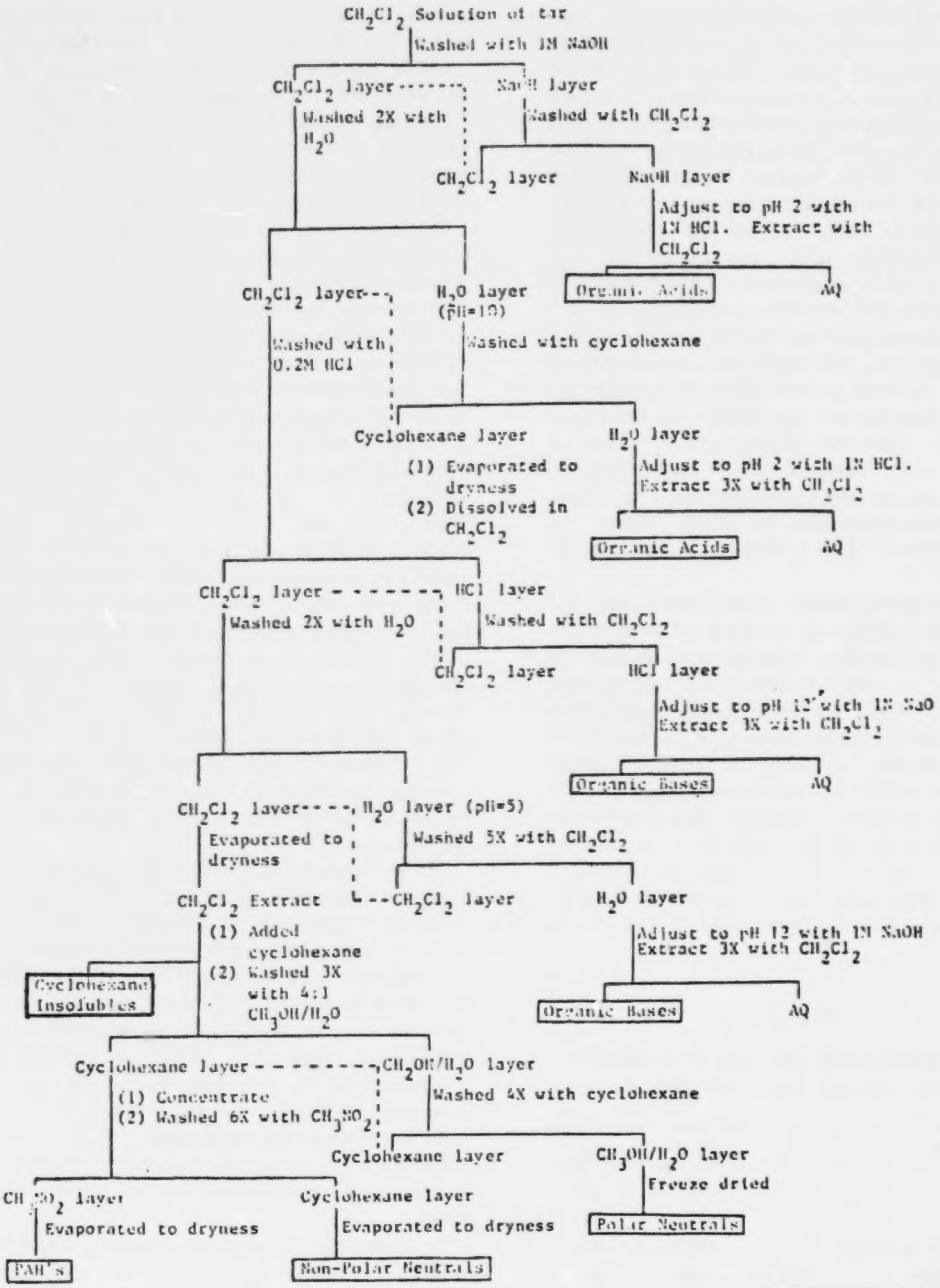
CH_2Cl_2 Solution of tar
Washed with 1M NaOH
CH_2Cl_2 layer
NaOH layer
Washed 2X with H_2O
Washed with CH_2Cl_2
CH_2Cl_2 layer
NaOH layer
Adjust to pH 2 with 1M HCl. Extract with CH_2Cl_2
Organic Acids
AQ
CH_2Cl_2 layer
H_2O layer (pH=10)
Washed with 0.2M HCl
Washed with cyclohexane
Cyclohexane layer
(1) Evaporated to dryness
(2) Dissolved in CH_2Cl_2
H_2O layer
Adjust to pH 2 with 1M HCl. Extract 3X with CH_2Cl_2
Organic Acids
AQ
CH_2Cl_2 layer
HCl layer
Washed 2X with H_2O
Washed with CH_2Cl_2
CH_2Cl_2 layer
HCl layer
Adjust to pH 12 with 1M NaOH Extract 3X with CH_2Cl_2
Organic Bases
AQ
CH_2Cl_2 layer
H_2O layer (pH=5)
Evaporated to dryness
Washed 5X with CH_2Cl_2
CH_2Cl_2 Extract
CH_2Cl_2 layer
H_2O layer
(1) Added cyclohexane
(2) Washed 3X with 4:1 CH_3OH/H_2O
Cyclohexane Insolubles
Adjust to pH 12 with 1M NaOH Extract 3X with CH_2Cl_2
Organic Bases
AQ
Cyclohexane layer
CH_3OH/H_2O layer
(1) Concentrate
(2) Washed 6X with CH_3NO_2
Washed 4X with cyclohexane
Cyclohexane layer
CH_3OH/H_2O layer
Freeze dried
Polar Neutrals
CH_3NO_2 layer
Evaporated to dryness
PAH's
Cyclohexane layer
Evaporated to dryness
Non-Polar Neutrals

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Figure 2. Tar sample partition scheme.

The latter approach seems more practical, particularly if fractions are to be derivatized or chromatographed further. The basic procedure adapted for use in our laboratories is depicted in Figure 2, and is a modification of a method utilized by Novotny[6] for air particulate extracts. Application of the scheme to three different gasifier coal tars produced the product distribution shown in Table 1. That the scheme provides generally good reproducibility was demonstrated by application of the process to identical aliquots from the same tar samples.

With the sample thus divided into chemically similar groups, derivatization and chromatographic techniques are applied as dictated by class properties or complexity of individual fractions. Thus the organic acid fraction is treated with diazomethane and dimethyl sulphate to convert carboxylic acids to esters and aromatic hydroxyls to methyl ethers. The compounds are then sufficiently volatile for gc analysis.

The remaining fractions are in most cases not amenable to direct gc analysis either because of the large number of components present or because of the presence of nonvolatile materials. Liquid chromatographic techniques are indicated here, especially hplc. This technique embraces virtually all forms of liquid chromatography, i.e., adsorption partition, ion-exchange and gel permeation, and is desirable chiefly because of the relatively high efficiencies obtainable with currently manufactured hplc columns. Although reverse-phase modes of chromatography have been shown to be very useful with regard to the separation of certain types of environmentally important compounds, the use of aqueous solvents is generally undesirable if the sample is to be recovered for further work. Consequently, we have explored primarily the use of adsorption and gel permeation modes as a means of further fractionating the partitioned samples.

TABLE 1

CLASS DISTRIBUTION OF COAL TAR SAMPLES AFTER SOLVENT PARTITION (WGT. %)

Sample	H-1	B-1	B-2
Acids	14.2	3.4	2.7
Bases	1.3	41.9	1.5
Cyclohexane Insolubles	13.6	13.5	4.4
Polar Neutrals	12.1	5.6	8.6
Non-Polar Neutrals	3.2	7.5	20.1
PNA Hydrocarbons	18.2	22.8	38.9

Silica gel columns provide separation of the components of a given fraction based on the relative polarities of the individual compounds. Columns can be easily tailored for specific use by varying the column dimensions, the nature (and hence activity) of the silica packing, and the diameter of the particles used. Thus to effect a rapid clean-up of the PNA fraction (Figure 2), a large particle (37-75 micron) column of modest efficiency is sufficient for effecting the separation of PNA compounds, as a group, from more polar, non-PNA materials. This chromatographic step enriches the PNA fraction by removing approximately 1/3 of the total mass associated with the fraction. This greatly reduces problems relating to the analysis of the PNA's themselves. A sample of this enriched fraction was analyzed at this point by gc-ms. The ion plot is shown in Figure 3. Although many individual PNA compounds were identified from the mass spectra generated from this run, a better resolved chromatogram is desirable particularly from a standpoint of quantitation.

Further separations can be accomplished by injection of the enriched fraction onto a high efficiency (10,000-15,000 plates/meter), silica column, and collecting individual cuts for gc-ms analysis. The results of this hplc run are shown in Figure 4. Detection of eluting components was accomplished by monitoring uv absorbance (254 nm). The gc-ms analysis of the collected and concentrated cuts is not yet available. Although silica gel columns were used here and can in all probability be applied to other fractions, other materials such as alumina or bonded phase columns may also prove effective.

Another chromatographic procedure can be utilized to simplify the complex fractions as obtained from the partition scheme. Gel permeation has been used by many workers[6,7] and has in the past been characterized by low efficien-

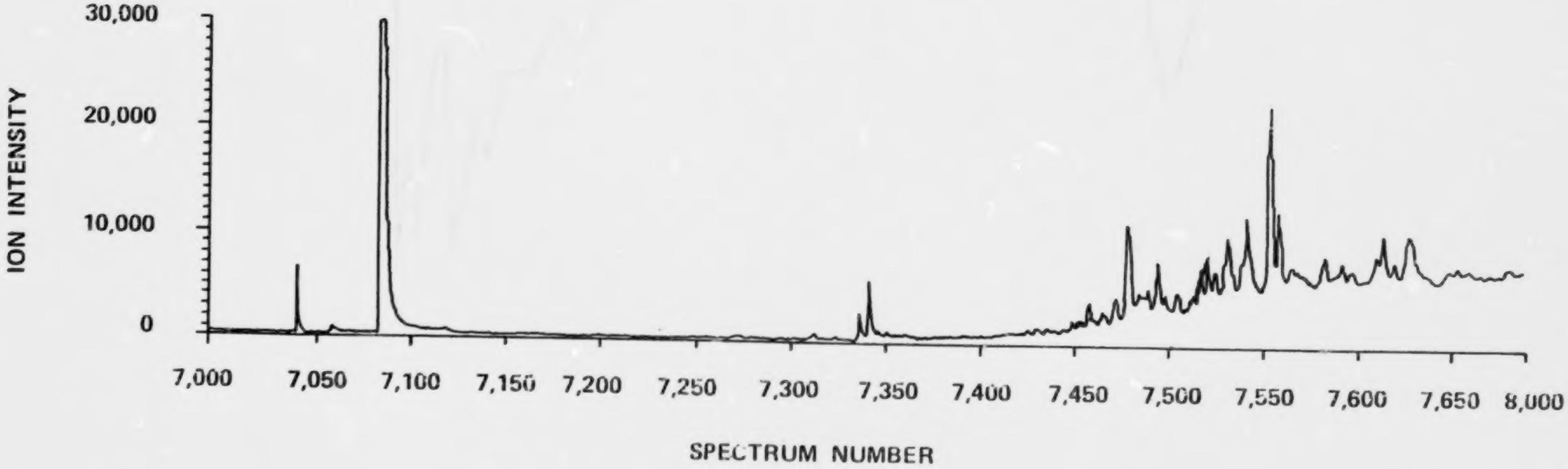

Figure 3. Ion plot of PNA enriched fraction. OV-101 capillary.

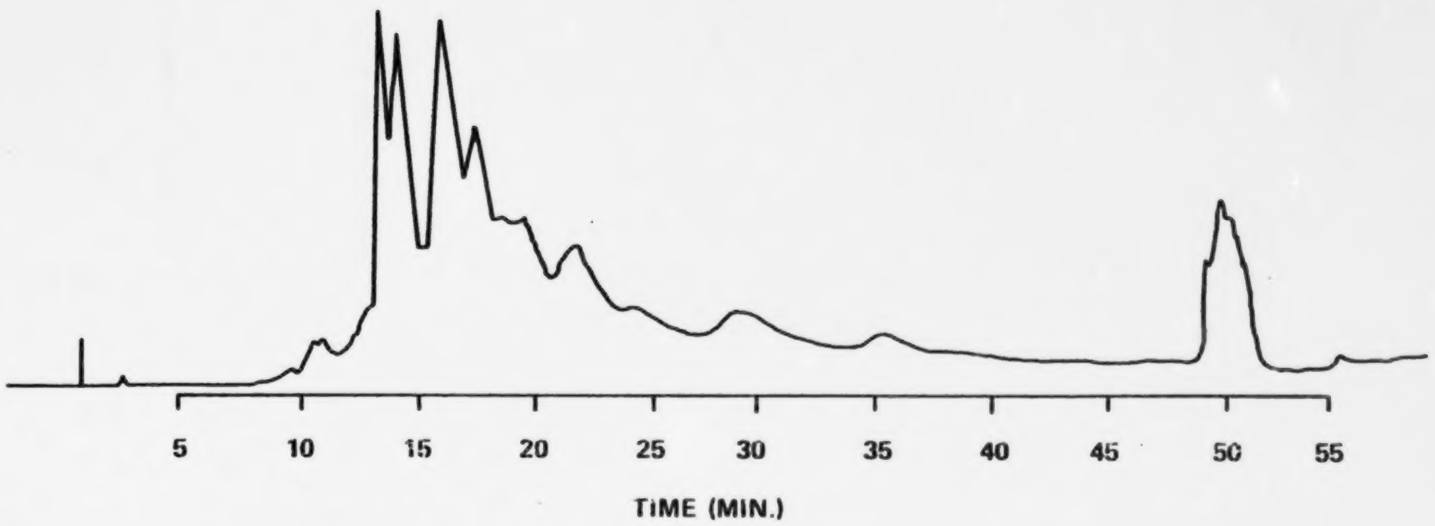

Figure 4. Hplc (silica) of PNA fraction.

cies and long run times. Recent developments in column technology now bring the advantages of hplc to this mode of chromatography. Thus fractions from the partition scheme can be subjected to gpc directly with compound separations made on the basis of molecular size. Since in a given chemical class molecular size correlates well with volatility, some information pertinent to subsequent gc-ms or ms analysis can be obtained from the chromatography. When the PNA fraction was chromatographed on a single gpc column, (μStyragel® - 100A pore size), the chromatogram depicted in Figure 5 was obtained. The large number of components and the continuum of molecular sizes combined to produce only a single undefined major peak, however arbitrary cuts of the column effluent will undoubtedly provide greatly simplified samples for subsequent analysis.

The coal gasification process produces byproduct water in sizeable quantities and, since this water can be used as recycle cooling water, methods for its purification are being ex-

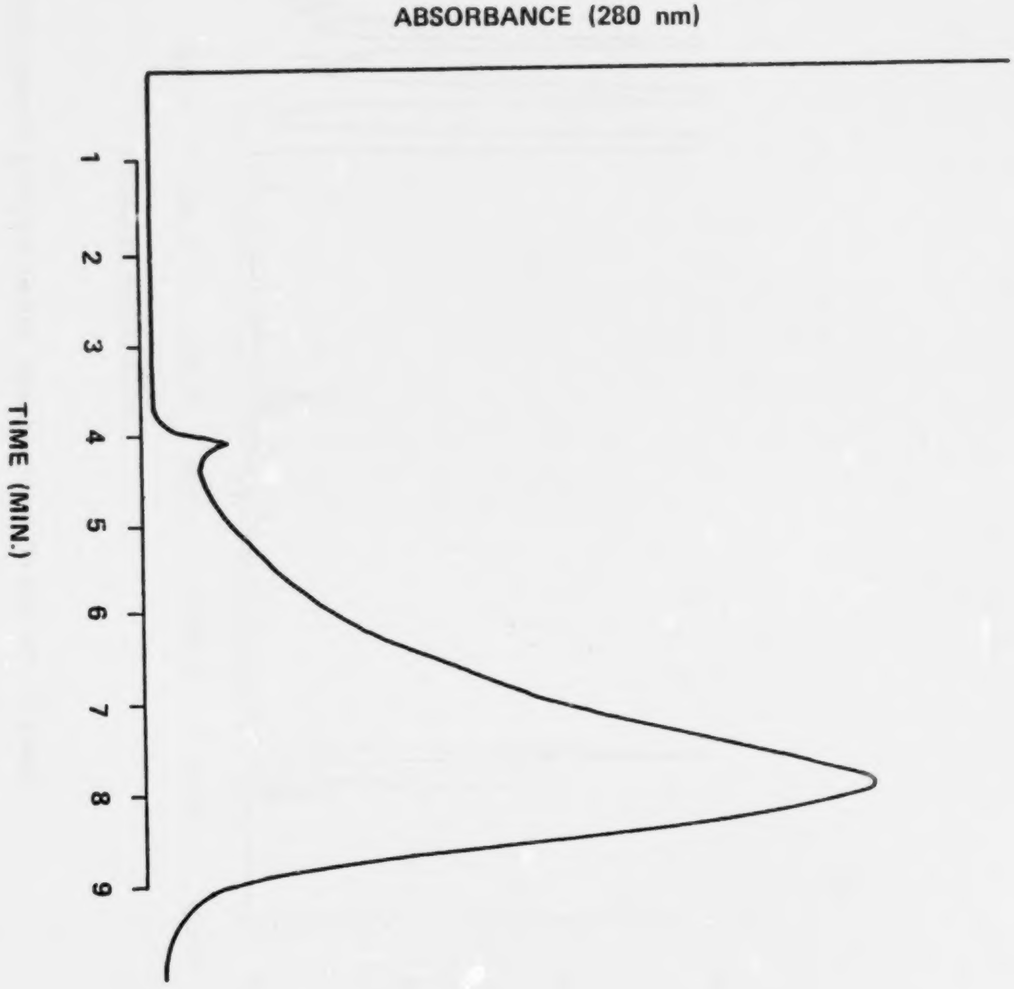

Figure 5. Gpc (μStyragel) of PNA enriched fraction.

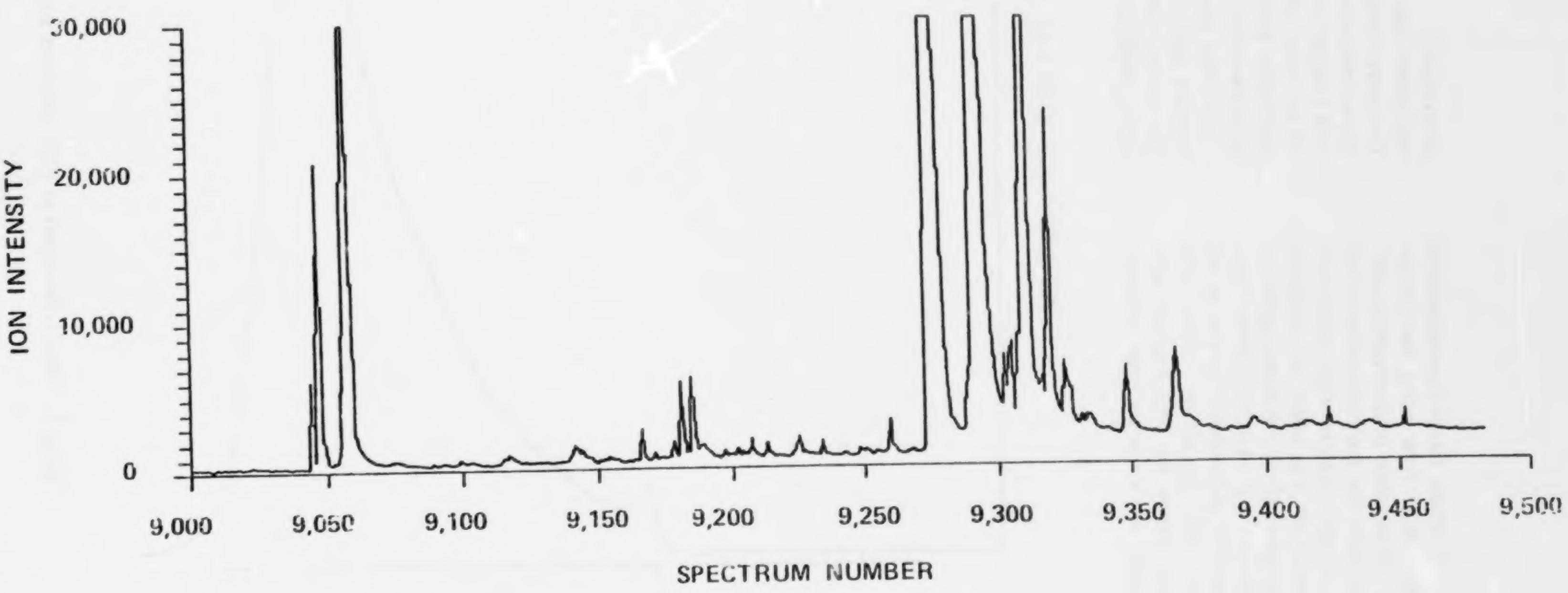

Figure 6. Ion plot of condensed water extract following derivatization Carbowax capillary.

plored. This involves a detailed knowledge of the contaminants which can comprise from 0.6-2.4 percent (by weight) of the condensate. This extractable material appears to be largely phenolic.[3] Thus after solvent extraction (methylene chloride) of a portion of the collected waters, the residue is subjected to treatment with diazomethane and dimethyl sulphate which converts the phenolic materials to aromatic methyl ethers. These compounds are amenable to high resolution gc-ms analysis, and can be thus analyzed without further processing. Treatment of a sample of condensate waters in our laboratories by the method described resulted in the TIC plot shown in Figure 6. Cursory examination of selected mass plots identified several aromatic alcohols including seven alkylated isomers of phenol. Other types of materials such as alkyl and aromatic ketones, carboxylic acids, and nitrogen-containing aromatics (1-2 ring) were also identified. Future runs will employ gc columns of increased resolution and selectivity. The methodology for the condensate waters appears adequate at this point for the tasks of identifying the contaminants of byproduct waters.

CONCLUSIONS

Although optimization of the methodological schemes presented above has yet to be finalized, the basic procedures have been shown to be practical and can be summarized as follows.

Volatiles: Methodology consists of collection of volatile components on polymer sorbents, transfer to high resolution gc-ms-comp systems for identification, and quantitation.

Nonvolatiles-Tars: Methodology consists of separating tars into groups of chemically similar materials by solvent partition. Organic acids are derivatized then analyzed by gc-ms. Other groups are further fractionated by hplc using either gpc or partition chromatography. Collected subfractions are then analyzed by gc-ms or ms.

Nonvolatiles-Waters: Methodology consist of derivatization of extracted material followe by gc/ms analysis.

Much work remains before the approache detailed here can be considered as complet and final. This is particularly true of the ta samples. Specific problems requiring additiona fundamental research efforts include the stud of materials that are too thermally labile or to nonvolatile for gc-ms analysis, and the problen of quantitation of individual components. Bot of these topics will be the subject of futur work relating to the analysis of environmentall important materials produced during co gasification.

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A COMPARISON OF TRACE ELEMENT ANALYSES OF NORTH DAKOTA LIGNITE LABORATORY ASH WITH LURGI GASIFIER ASH AND THEIR USE IN ENVIRONMENTAL ANALYSES

Mason H. Somerville
James L. Elder
Engineering Experiment Station
University of North Dakota
Grand Forks, North Dakota

Abstract

A series of analyses of laboratory prepared ashes of Dunn County, North Dakota, lignite are compared with analyses of Mercer County, North Dakota, lignite gasifier ash from SASOL gasification test for 73 elements. The analyses demonstrate that a need for laboratory ashing technique that simulates gasifier ash probably exists. Of the 73 elements, 33 were found to be common to the leachate of both the gasifier and laboratory ash samples; nine of the 33 were more leachable in the gasifier ash. Approximately 50 of the 73 elements are found in both coals while approximately 20 elements were below the detection limit of 0.1 ppm in both coals.

The use of this data for environmental assessment of groundwater impact is analyzed. It is concluded that this data probably cannot be used to support existing analytical groundwater models due to system complexities and unknowns. An alternative worst case environmental analysis is presented. It is recommended that worst case analyses be pursued rather than sophisticated analytical modeling techniques.

INTRODUCTION

The continuing energy problem is gradually forcing the major investors and industries of the United States to turn to coal conversion technologies for the development of sources of supply of liquid and gaseous fossil fuels and feedstocks. Although the time scale and extent of this development are unknown, it is likely in the author's view, that several coal conversion facilities will be operable by the end of the century. These facilities will probably include major 250 MMSCFD dry ash Lurgi gasification facilities.

Presently, plans for four such facilities are at the detailed design stage. These facilities are El Paso Gasification Company, Wesco Coal Gasification Company, ANG Coal Gasification Company, and Natural Gas Pipeline Company of America. El Paso and Wesco are located in New Mexico while ANG and Natural are located North Dakota. All four have filed Environmental Assessment Reports. The Department of the Interior (DOI) has issued final Environmental Impact Statements for El Paso and Wesco. DOI has issued a draft Environmental Impact Statement for ANG. Natural has issued only an Environmental Assesment Report. All of the companies have studied, to varying degrees, the environmental impacts associated with disposal of the gasifier ash and its entrained water. This paper addresses one of those impacts.

The work reported here deals with the possible leaching of the trace elements from disposed gasifier ash. Although it may be possible to mitigate this potential impact to within acceptable limits through the use of disposal techniques, it is difficult, if not impossible, to conclusively demonstrate that the disposed ash and sludges will behave in a given manner once actually disposed of in the mined area. This is true, in spite of the current mathematical models that exist, largely because of widely varying boundary conditions and the very complex chemical systems that may exist in the post-mining environment.

Because of these difficulties it is probably advisable to attack the question of potential environmental imact utilizing a worst case approach. This approach does not address the question of actual impact, but does allow one to estimate the maximum impact that can reasonably be expected.

The fate of trace and major constituents during gasification has been addressed by Somerville, et al. (1977)[1], (1976)[2], and by Attari, et al. (1976)[3], (1973)[4]. At the conclusion of the work cited above, the authors noted that the analyses of the laboratory prepared ashes and its leachates were considerably different than those of the Lurgi generated ashes and its leachates.

Data are presented below which specifically compare laboratory and actual gasifier ash and their leachates.

It should be pointed out that the data collected were for the purpose of supporting two different Environmental Assessment Reports which at the time of the data collection were unrelated. Consequently, the authors did not have the opportunity to gather all the control data that are desirable.

OBJECTIVES

The study, under which this data was generated, was made to assess the environmental impact associated with a 250 MMSCFD Lurgi dry ash coal gasification facility utilizing Dunn County, North Dakota lignite. This paper assesses the applicability and use of laboratory ashing techniques to determine the probable trace element emissions from a coal gasification facility.

METHODS

General

Two different lignites, Mercer County and Dunn County, North Dakota, were analyzed for major and minor elemental constituents. The Mercer lignite sample was obtained from the coal gasified as part of an operational test at Sasolburg, South Africa (SASOL). The Dunn County samples were obtained by coring as part of a resource evaluation program. Dunn County and Mercer County, North Dakota are approximately 45 miles apart; both are in the Fort Union Coal Reserve (e.g., the same geological strata).

The Mercer County lignite ash samples utilized were obtained during the SASOL test. The Dunn County lignite samples were ashed and the ash analyzed using ASTM D2795-69, "Mineral Analysis of Coal and Coke Ash". Leachate tests were performed on both ash samples.

The Sasolburg Test

The chemical analyses of the Mercer County lignite reported were taken from samples obtained when 12,000 tons were gasified in the Lurgi gasifier at Sasolburg, South Africa in 1974 by Michigan-Wisconsin Gas Pipeline Company. Samples of the lignite charged to the gasifier, and the ash from the gasifier were obtained.

The coal feed rate during each test was approximately 26 tons/hr with a mass balance test lasting for about 8 hours. The following sample collection intervals were used: hourly for the coal, and each dump for the gasifier ash.

Analytical Procedures

The sample analyses were performed using the following techniques: spark source mass spectrometry (SSMS), atomic absorption (AA), flameless atomic absorption (FAA), ion-selective electrode methods (IE), colorimetric (C), standard mineral analysis (MA), and several wet chemical methods (WC). The details of the procedures and methods used are described in Appendix A. All raw data obtained from the tests and referenced in this paper may be found in Somerville et al. (1976).[1]

Leaching Study

Since it was suspected that many of the elements found in coal would probably be retained in the gasifier ash and plans called for the disposal of the ash in the mined area, an experiment was designed to study the leaching characteristics of the ash (both laboratory and SASOL). The methods selected purposefully attempted to maximize the quantity of the element leached in an attempt to predict the upper bound of the impact. The general method consisted of grinding the ash to a fine powder, and refluxing a sample for 16 to 24 hours at the boiling point of demineralized water. This is thought to yield the worst case (maximum leachate concentration) because:

1. Refluxing subjects the ash to far more water than the annual rainfall ever would. It may take many years before moisture ever reaches the buried ash.
2. The use of distilled-demineralized water subjects the ash to harsher leaching conditions than the actual groundwater (which is basic) is expected to.
3. The refluxing of the leachate at the boiling point of water greatly increases the solubility of the elements in the solvent. Groundwater temperatures are considerably lower than this.
4. The procedure used small particle size

samples, which increases the solubility rather than the ash of much larger particle size resulting from operation.

Table A-1 of Appendix A lists the element and analytical method used for determination of the concentration of that element in the particular sample. The following abbreviations were used to identify the type of analysis:

SSMS - spark source mass spectrometry
AA - atomic absorption
FAA - flameless atomic absorption with double gold amalgamation
C - colorimetric
IE - USGS method specific ion electrode
MA - ASTM-2795-69 - mineral analysis
U - ultimate analysis
G - gravimetric
NR - not reported, if present
<0.1 ppm wt gasifier ash
<0.001 μg/ml gasifier ash leach

The leaching procedure which was used consisted of the following steps:

1. The samples were crushed to 60 mesh and the 10 g of material being examined were weighed. Coal samples were weighed air dry and ash samples were weighed dry. 50 ml of deionized water was added.
2. The above mixture was refluxed for 16 to 24 h at the boiling point of water. The solution was filtered and/or decanted until clear and the laboratory examination performed on the clear solution.
3. The liquid to solid ratio (5 to 1) was maintained if a larger quantity was used for leaching.

RESULTS AND DISCUSSION

Elemental Analyses were run on the following samples:

*Mercer County lignite and its ash from the SASOL gasification test. (See Table 1)

*Mercer County lignite ash leachate from the SASOL gasification test ash. (See Table 2)

Dunn County lignite and its laboratory ash for two coal samples: 4411 and 4413. (See Table 2)

Since gasifier ash using Dunn County lignite was not available for leaching tests, laboratory ash was used in its place. Analyses were performed, on each of the samples identified above. The results of those analyses are presented in Tables 1 and 2.

The data of Table 2 can be reduced by calculating the percent leachable which is determined with the following formula:

% leachable = (CL * 5/CA) * 100

where

CL = concentration of element in the leachate, μg/ml
CA = concentration of the element in the ash, ppm
5 = ratio of water leach base to material weight

Table 3 presents the leachable percentages for each of the 73 elements and also reports the ratio of Mercer gasification ash percentage leachable to Dunn's laboratory ash percent leachable.

Tables 4 and 5 present the upper bounds for the estimated effluent rates from a proposed gasification facility (Somerville et al (1976)[2]) and the maximum leachate rates that can be expected. Table 4 presents the elements found to be more soluble from gasifier ash, Table 5, elements more soluble from the laboratory prepared ash. Table 6 presents the ratio of the elements for the two lignites, their ashes and ash leachates. Table 7 examines the similarity of element concentrations between the lignites, their ashes and ash leachates by reporting the cumulative probability of occurrence as a function of ratio range.

A visual examination of the element concentrations of Table 1 for the Dunn and Mercer lignites reveals that they are similar. This observation is also supported by our experience with Fort Union Lignites which indicates that they are generally similar (Sondreal et al. (1968)[5]). It is not obvious that the ash element concentrations reported in Table 1 are similar. This may be due to the different environment that Mercer ash experienced during gasification as opposed to laboratory ashing environment. The difference becomes even more pronounced in the ash leachate data reported in Table 2. This difference is further amplified when the percentage of the element that is leachable is calculated and the ratio of the Mercer to Dunn percentage leachable is calculated. These

TABLE 1

COMPARISON OF TRACE ELEMENT AND MAJOR CONSTITUENTS IN MERCER COUNTY AND DUNN COUNTY NORTH DAKOTA LIGNITE AND THEIR ASHES, ppm

Element	Dry Coal[a,b]				Ash[b]		
	Mercer Co.	Dunn Co.			Mercer Co.	Dunn Co.	
		4411	4413	Avg./12 Samples		4411	4413
Ag	<0.1			<0.1	<1	<0.3	<0.3
Al	5,666[c]			6,697[d,e]	63,400[d]	94,000[f]	110,000[f]
As	8	11	9	10.13	74	36	30
Au	<0.1			<0.1			
B	56	135	39	62.95	1,680[f]	380	450
Ba	616[f]	113	81	229.82	8,270[f]	3,800[f]	10,200[f]
Be	0.27	0.8	0.3	0.31	6	0.3	0.5
Bi	<0.1			<0.1		0.3	0.3
Br	0.27	1.5	0.75	1.71	3	0.3	0.6
Ca	16,225[c]			16,108[d,e]	181,600[d]	236,000[f]	300,000[f]
Cd	<1[f]	<0.15[f]	<0.15[f]	0.21[f]	0.5[f]	<1	<1
Ce	34.6	24	11	14.06	190	37	85
Cl	26.7	92	39	46.62	67	15	62
Co	1.2	10.7	4.5	4.98	13	6	6
Cr	5.3	490	7.5	65.26	140	35	17
Cs	4	1.1	<0.15	0.26	9	0.9	0.4
Cu	10.6	73	17	22.92	27	18	27
Dy	0.67			<0.1	8	2	3
Er	<0.1			<0.1	4	0.5	1
Eu	0.4	0.3	0.3	0.26	4	0.5	0.8
F	29.3[g]	25[g]	24[g]	20.83[g]	191[g]	220[g]	250[g]
Fe	7,936[c]			7,216[d,e]	78,800[d]	Mc[h]	Mc[h]
Ga	5.3	8	3	4.58	53	12	0.5
Gd	0.8	<0.1	<0.1	0.23	5	0.9	2
Ge	0.27	3	0.9	0.60	2	4	7
Hf	<0.1			<0.1	4	0.9	0.9
Hg	0.2[i]	0.14[i]	0.11[i]	0.20[i]	0.55[i]	0.02[i]	0.04[i]
Ho	0.4			<0.1	5	0.6	0.9
I	0.13	0.15	0.3	0.39	2		
Ir	<0.1			<0.1			

TABLE 1 (Continued)

Element	Dry Coal[a,b]				Ash[b]		
	Mercer Co.	Dunn Co.			Mercer Co.	Dunn Co.	
		4411	4413	Avg./12 Samples		4411	4413
K	268[c]			462[d,e]	4,600[d]	11,200[f]	8,200[f]
La	16	9	1.5	5.83	74	16	34
Li	0.67	6	1.5	1.24	45	8	20
Lu	<0.1			<0.1	0.5	0.1	0.2
Mg	3,877[c]			5,039[d,e]	42,100[d]	Mc[h]	Mc[h]
Mn	70.7	383	38	248.90	760	Mc	210
Mo	4	43	63	22.22	12	6	10
Na	6,994[c]			2,395[d,e]	58,604[d]	114,000[f]	174,000[f]
Nb	4	11	1.5	3.86	37	10	17
Nd	2.7	0.8	0.8	0.96	18	3	8
Ni	6.7	31	15	11.55	25	30	15
Os	<0.1			<0.1			
P	236[c]			131[d,e]	3,500[d]	Mc[h]	Mc[h]
Pb	2.7	8	1.5	5.44	58	32	33
Pd	<0.1			<0.1			
Pr	1.3	1.5	0.5	0.85	8	2	4
Pt	<0.1			<0.1			
Rb	6.7	12	1.5	4.13	35	17	4
Re	<0.1			<0.1			
Rh	<0.1			<0.1			
Ru	<0.1			<0.1			
S	11,956[c]			13,000[e,j]	12,600[d]	29,300[k]	18,400[k]
Sb	0.27	0.9	0.45	0.31	4	1	2
Sc	8	9	11	7.98	33	16	15
Se	0.4	1.5	0.6	0.85	0.5	0.2	1
Si	9,114[c]			11,011[d,e]	118,100[d]	138,000[f]	128,000[f]
Sm	1.07	0.46	0.45	0.47	7	2	2
Sn	0.27	14	1.5	5.08	4	2	7
Sr	1,729[f]	918	1,050	1,029.27	12,900[f]	40,000[f]	26,000[f]
Ta				0.1	≤0.2	≤0.1	≤0.2

TABLE 1 (Continued)

Element	Dry Coal[a,b]				Ash[b]		
	Mercer Co.	Dunn Co.		Avg./12 Samples	Mercer Co.	Dunn Co.	
		4411	4413			4411	4413
Tb	0.67	<0.1	<0.1	0.15	3	0.6	1
Te	0.27			<0.1	≤0.3	≤0.2	≤0.2
Th	4	9	1.5	3.64	45	8	31
Ti	193[c]			301[d,e]	3,420[d]	610	Mc[h]
Tl	<0.1			<0.1	5		
Tm	<0.1			<0.1	0.5	0.2	0.2
U	4	6	1.5	3.15	7	7	8
V	21.3	61	14	21.93	150	28	20
W	<0.1	3	0.6	0.58	2	0.9	0.8
Y	13.3	54	42	23.11	320	34	48
Yb	<0.1			<0.1	4	1	2
Zn	6.7	23	23	10.87	10	70	30
Zr	85.3	184	68	68.42	520	100	94

[a] Analysis are reported on dry coal basis.

[b] Method of analysis, spark source mass spectrometry; unless noted otherwise. Detection limits for coal and gasifier ash at 0.1 ppm.

[c] Sondreal, E.A., Wayne R. Kube, James L. Elder,[5] "Analysis of the Northern Great Plains Province Lignites and Their Ash: A Study of Variability," U.S. Dept. of Interior, Bureau of Mines, RI 7158, 1968, analytical data taken from Tables 3 and 4, p.8, average of 22 samples from Indianhead Mine, Mercer County, N.D.

[d] Method of analysis, ASTM, D 2795-69, Mineral Analysis of Coal and Coke Ash, part 19, 1974.

[e] Average of four lower bed composites, Nos. 3,4,5,6, Report of Paul Weir Co. to Natural Pipeline Co. of America, October 27, 1972.

[f] Method of analysis, atomic absorption vs. aqueous standards.

[g] Method of analysis, U.S.G.S. method, ion-selective electrode.

[h] Analysis not performed on these ashes. Composite of lower beds 3,4,5 and 6 is available and gives: iron, 64834 ppm; titanium, 2704 ppm; magnesium, 45274 ppm; and phosphorous, 1177 ppm.

[i] Method of analysis, flameless atomic absorption (double gold amalgamation).

[j] Method of analysis, ASTM D 271-68, Laboratory Sampling and Analysis of Coal and Coke, part 19, 1969.

[k] Gravimetric.

TABLE 2

ASH AND ASH LEACHATE ANALYSES, MERCER COUNTY LIGNITE AND DUNN COUNTY LIGNITE

	Mercer County Lignite SASOL Gasification Test		Dunn County Lignite			
Element	Ash (ppm)	Leachate (µg/ml)	4411 Lab Ash (ppm)	Leachate (µg/ml	4413 Lab Ash (ppm)	Leachate (µg/ml)
Ag, silver	≤1		≤0.3		≤0.3	
Al, aluminum	63,400	230	94,000	8	110,000	130
As, arsenic	74	3	36	0.02	30	0.07
Au, gold						
B, boron	1,680	36.6	380	13.5	450	12.5
Ba, barium	8,270	0.01	3,800	<1	10,200	<1
Be, beryllium	6		0.3		0.5	
Bi, bismuth			0.3		0.3	
Br, bromine	3	0.3	0.3	0.01	0.6	0.01
Ca, calcium	181,600[a]	19	236,000	380	300,000	95
Cd, cadmium	0.7		<1	<0.01	<1	<0.01
Ce, cerium	190		37	0.007	85	
Cl, chlorine	67	38	15	2	62	3
Co, cobalt	13	0.02	6	≤0.009	6	≤0.03
Cr, chromium	140	0.07	35	0.2	17	0.2
Cs, cesium	9	0.02	0.9	0.06	0.4	0.04
Cu, copper	27	0.05	18	0.2	27	0.4
Dy, dysprosium	8		2		3	
Er, erbium	4		0.5		1	
Eu, europium	4		0.5		0.8	
F, fluorine			220	<1.5	250	2.8
Fe, iron	78,800[a]	0.3	MC[b]	0.5	MC[b]	1
Ga, gallium	53	1	12	0.02	0.5	0.5
Gd, gadolinium	5		0.9		2	
Ge, germanium	2	0.005	4	0.004	7	≤0.03
Hf, hafnium	4		0.9		0.9	
Hg, mercury			0.02	0.002	0.04	0.003
Ho, holmium	5		0.6		0.9	
I, iodine	2	0.2				
Ir, iridium						
K, potassium	4,600[a]	110	11,200	414	8,200	393

TABLE 2 (Continued)

	Mercer County Lignite SASOL Gasification Test		Dunn County Lignite			
Element	Ash (ppm)	Leachate (μg/ml)	4411 Lab Ash (ppm)	Leachate (μg/ml)	4413 Lab Ash (ppm)	Leachate (μg/ml)
La, lanthanum	74		16	0.006	34	
Li, lithium	45	0.002	8	≤0.07	20	≤0.07
Lu, lutetium	0.5		0.1		0.2	
Mg, magnesium	42,100[a]	0.2	MC[b]	1	MC[b]	8
Mn, manganese	760	0.006	MC	0.04	210	0.2
Mo, molybdenum	12	1	6	1	10	2
Na, sodium	58,604[a]	7,100	114,000	8,600	174,000	12,700
Nb, niobium	37		10		17	
Nd, neodymium	18		3		8	
Ni, nickel	25	0.009	30	0.06	15	0.05
Os, osmium						
P, phosphorous	3,500[a]	0.9	MC[b]	1	MC[b]	1
Pb, lead	58	0.007	32	0.02	33	<0.02
Pd, palladium						
Pr, praseodymium	8		2	0.003	4	
Pt, platinum						
Rb, rubidium	35	1	17	1	4	0.7
Re, rhenium						
Rh, rhodium						
Ru, ruthenium						
S, sulfur	12,600[a]	1,205	29,300	3,804	18,400	3,804
Sb, antimony	4	0.01	1		2	
Sc, scandium	33	≤0.003	16	≤0.01	15	≤0.03
Se, selenium	0.5	0.02	0.2	<0.009	1	≤0.09
Si, silicon	118,100[a]	900	138,000	<5	128,000	<5
Sm, samarium	7		2		2	
Sn, tin	4	0.003	2		7	
Sr, strontium	12,900	0.09	40,000	43	26,000	45
Ta, tantallum	≤0.2		≤0.1		≤0.2	
Tb, terbium	3		0.6		1	
Te, tellurium	≤0.3		≤0.2		≤0.2	

TABLE 2 (Continued)

	Mercer County Lignite SASOL Gasification Test		Dunn County Lignite			
Element	Ash (ppm)	Leachate (μg/ml)	4411 Lab Ash (ppm)	Leachate (μg/ml)	4413 Lab Ash (ppm)	Leachate (μg/ml)
Th, thorium	45		8		31	
Ti, titanium	3,420[a]	0.1	610	0.3	MC[b]	0.4
Tl, thallium	5					
Tm, thulium	0.5		0.2		0.2	
U, uranium	7		7		8	
V, vanadium	150	8	28	0.3	20	0.2
W, tungsten	2	0.04	0.9	0.03	0.8	0.05
Y, yttrium	320	≤0.02	34		48	
Yb, ytterbium	4		1		2	
Zn, zinc	10	0.02	70	0.1	30	0.4
Zr, zirconium	520		100	0.3	94	

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[a] Method of Analysis ASTM D2795-69, Mineral Analysis of Coal and Coke Ash, Part 19, 1974.

[b] Analyses not performed on these ashes. Composite of lower beds 3, 4, 5, and 6 is available and gives: iron, 64834 ppm; titanium, 2704 ppm; magnesium, 45274 ppm; and phosphorous, 1177 ppm.

TABLE 3

PERCENT OF ELEMENT LEACHABLE FROM MERCER COUNTY GASIFIER ASH AND DUNN COUNTY LIGNITE LABORATORY ASH

Element	Mercer County SASOL Ash	Dunn County Lab Ash	Ratio
	% Leachable	% Leachable (Avg. of 4411, 4413)	Mercer/Dunn
Ag, silver	0.5		
Al, aluminum	1.8	0.32	5.63
As, arsenic	20.3	0.74	27.43
Au, gold			
B, boron	10.9	15.9	0.69
Ba, barium	0.0006	<0.09	>0.01
Be, beryllium			
Bi, bismuth			
Br, bromine	50	13	3.85
Ca, calcium	0.05	0.49	.102
Cd, cadmium		<5	
Ce, cerium		0.09	
Cl, chlorine	283[a]	46	
Co, cobalt	0.77	1.6	0.48
Cr, chromium	0.25	4.4	0.06
Cs, cesium	1.1	42	0.03
Cu, copper	0.93	7	0.13
Dy, dysprosium			
Er, erbium			
Eu, europium			
F, fluorine	10.2	4.5	2.27
Fe, iron	0.002	<0.4	>0.01
Ga, gallium	9.4	5.4	1.74
Gd, gadolinium			
Ge, germanium	1.3	≤1.3	≥1
Hf, hafnium			
Hg, mercury	0.91	4.4	0.21
Ho, holmium			
I, iodine	50		
Ir, iridium			
K, potassium	12	21.3	0.56
La, lanthanum		0.19	

TABLE 3 (Continued)

	Mercer County SASOL Ash	Dunn County Lab Ash	Ratio
	% Leachable	% Leachable (Avg. of 4411, 4413)	Mercer/Dunn
Li, lithium	0.02	11	0.002
Lu, lutetium			
Mg, magnesium	0.002		
Mn, manganese	0.004	≤0.25	≥0.02
Mo, molybdenum	41.7	92	0.45
Na, sodium	60.6	37.1	1.63
Nb, niobium			
Nd, neodymium			
Ni, nickel	0.18	1.4	0.13
Os, osmium			
P, phosphorous	0.13	<0.5	>0.26
Pb, lead	0.06	0.31	0.19
Pd, palladium			
Pr, praseodymium		.75	
Pt, platinum			
Rb, rubidium	14.3	59	0.24
Re, rhenium			
Rh, rhodium			
Ru, ruthenium			
S, sulfur	47.8	84	0.57
Sb, antimony	1.3		
Sc, scandium	0.05	<0.66	>0.08
Se, selenium	20	<34	>0.59
Si, silicon	3.8	<0.02	>190
Sm, samarium			
Sn, tin	0.4		
Sr, strontium	0.003	0.71	0.004
Ta, tantallum			
Tb, terbium			
Te, tellurium			
Th, thorium			
Ti, titanium	0.01	<2.3	>0.004

TABLE 3 (Continued)

Element	Mercer County SASOL Ash % Leachable	Dunn County Lab Ash % Leachable (Avg. of 4411, 4413)	Ratio Mercer/Du
Tl, thallium			
Tm, thulium			
U, uranium			
V, vanadium	26.7	5.2	5.13
W, tungsten	10	24	0.42
Y, yttrium	0.03		
Yb, ytterbium			
Zn, zinc	1	3.7	0.27
Zr, zirconium		1.5	

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[a] Irrational number, unexplained error.

TABLE 4

ESTIMATED MAXIMUM SOLUTION RATES FOR ELEMENTS MORE SOLUBLE FROM GASIFIER ASH[a]

	Ratio of to Mercer/Dunn Ash Leachate Rates	Dunn Co. Estimated Effluent[b] (lbs/day)	Laboratory Dunn County Ash, % Leachable	Estimated[b] Maximum Leachate Rate (lbs/day)
aluminum	5.63	243,600	0.32	780
arsenic	27.43	339	0.74	2.5
bromine	3.85	61	13	7.9
fluorine	2.27	513	4.5	23.1
gallium	1.74	168	5.4	9.1
germanium	>1.0	22	≤1.3	≤0.3
silicon	>190	393,200	<.02	78.6
sodium	1.63	86,000	37.1	31,906
vanadium	5.13	800	5.2	41.6

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[a] Mercer County coal processed at Sasolburg, South Africe.

[b] Based upon Somerville, et al (1976)[1]. Data is for a 250 MMSCFD Dry Ash Lurgi Gasification Plant.

TABLE 5

ESTIMATED MAXIMUM SOLUTION RATES FOR ELEMENTS MORE LEACHABLE FROM LABORATORY PREPARED ASH[a]

Element	Ratio of Mercer to Dunn Ash Leachate	Dunn Co. Estimated Effluent[b] (lbs/day)	% Leachable	Estimated Maximum Leachate Rate[b] (lbs/day)
boron	0.69	2,303.5	15.9	366.3
barium	>0.01	8,188.7	<0.09	7.4
calcium	.102	588,800	0.49	2,885
cobalt	0.48	178.19	1.6	2.9
chromium	0.06	2,349.5	4.4	103.4
cesium	0.03	9.48	42	4.0
copper	0.13	789.7	7	55.3
iron	>0.01	236,250.5	<0.4	<1,053.0
mercury	0.21	0.10	4.4	0.0
potassium	0.56	16,650.2	21.3	3,546.5
lithium	0.002	45.29	11	5.0
manganese	>0.02	9,098.6	≤0.25	≤22.75
molybdenum	0.45	691.9	92	636.5
nickel	0.13	397.1	1.4	5.6
phosphorous	>0.26	4,658.4	<0.5	<23.3
lead	0.19	177.01	0.31	0.5
rubidium	0.24	147.62	59	87.1
sulfur	0.57	56,048.9	84	47,081.1
scandium	>0.08	288.18	<0.66	<1.9
selenium	>0.59	4.32	<34	<1.5
strontium	0.004	37,815.9	0.71	268.5
titanium	>0.004	9,827.4	<2.3	<226.0
tungsten	0.42	21.37	24	5.1
zinc	0.27	299.3	3.7	11.1

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[a] Dunn County Coal, samples 4411 and 4413, processed in the laboratory.

[b] Based upon Somerville et al (1976)[1]. Data is for a 250 MMSCFD Dry Ash Lurgi Gasification Plant.

TABLE 6

RATIO OF ELEMENT CONCENTRATION IN MERCER COUNTY LIGNITE, ASH AND ASH LEACHATE TO THOSE OF DUNN COUNTY

Element	Lignite[a]	Ash[a]	Ash Leachate
Ag, silver	1.00[b,c]	3.00	N
Al, aluminum	0.85[c]	0.62	5.63
As, arsenic	0.80	2.24	27.43
Au, gold	1.00[c]	N	N
B, boron	0.64	4.05	0.69
Ba, barium	6.35	1.18	>0.01
Be, beryllium	0.49	15.00	N
Bi, bismuth	1.00[c]	N	N
Br, bromine	0.24	6.66	3.85
Ca, calcium	1.01[c]	0.68	.102
Cd, cadmium	6.67	0.50	N
Ce, cerium	1.98	3.11	N
Cl, chlorine	0.41	1.74	N
Co, cobalt	0.16	2.17	0.48
Cr, chromium	0.02	5.38	0.06
Cs, cesium	6.40	13.85	0.03
Cu, copper	0.24	1.20	0.13
Dy, dysprosium	6.70[c]	3.20	N
Er, erbium	1.00[c]	5.33	N
Eu, europium	1.33	6.15	N
F, fluorine	1.20	0.81	2.27
Fe, iron	1.10[c]	N	>0.01
Ga, gallium	0.96	8.48	1.74
Gd, gadolinium	8.00	3.45	N
Ge, germanium	0.14	0.36	≥1.00
Hf, hafnium	1.00[c]	4.44	N
Hg, mercury	1.60	1.83	0.21
Ho, holmium	4.00	6.67	N
I, iodine	0.58	N	N
Ir, iridium	1.00[c]	N	N
K, potassium	0.58[c]	0.47	0.56
La, lanthanum	3.05	2.96	N
Li, lithium	0.18	3.21	0.002
Lu, lutetium	1.00[c]	3.33	N
Mg, magnesium	0.77[c]	N	N

TABLE 6 (Continued)

Element	Lignite[a]	Ash[a]	Ash Leachate
Mn, manganese	0.34	3.62	≥0.02
Mo, molybdenum	0.08	1.50	0.45
Na, sodium	2.92[c]	0.41	1.63
Nb, niobium	0.64	2.74	N
Nd, neodymium	3.38	3.27	N
Ni, nickel	0.29	1.11	0.13
Os, osmium	1.00[c]	N	N
P, phosphorous	1.80[c]	N	>0.26
Pb, lead	0.57	1.78	0.19
Pd, palladium	1.00[c]	N	N
Pr, praseodymium	1.30	2.67	N
Pt, platinum	1.00[c]	N	N
Rb, rubidium	0.99	3.33	0.24
Re, rhenium	1.00[c]	N	N
Rh, rhodium	1.00[c]	N	N
Ru, ruthenium	1.00[c]	N	N
S, sulfur	0.92[c]	0.53	0.57
Sb, antimony	0.40	2.67	N
Sc, scandium	0.80	2.13	>0.08
Se, selenium	0.38	0.83	>0.59
Si, silicon	0.83[c]	0.89	>190
Sm, samarium	2.35	3.50	N
Sn, tin	0.03	0.89	N
Sr, strontium	1.76	0.39	0.004
Ta, tantallum	N	1.33	N
Tb, terbium	6.70	3.75	N
Te, tellurium	2.70[c]	1.50	N
Th, thorium	0.76	2.31	N
Ti, titanium	0.64[c]	5.61	>0.004
Tl, thallium	1.00[c]	N	N
Tm, thulium	1.00[c]	2.50	N
U, uranium	1.07	0.93	N
V, vanadium	0.57	6.25	5.13
W, tungsten	0.06	2.35	.42
Y, yttrium	0.28	7.80	N
Yb, ytterbium	1.00[c]	2.67	N

TABLE 6 (Continued)

Element	Lignite[a]	Ash[a]	Ash Leachate
Zn, zinc	0.29	0.20	0.27
Zr, zirconium	0.68	5.36	N

[N] Not calculable due to missing data.

[a] Calculated on the basis of the average of 4411 and 4413 unless otherwise noted.

[b] Number calculated on basis of a less than or greater than number. See tables 1 and 3.

[c] Calculated on the basis of an average of 12 samples instead of an average of 4411 and 4413.

TABLE 7

CUMULATIVE PROBABILITY OF COMMON OCCURANCE OF ELEMENTS, IN MERCER AND DUNN COUNTY LIGNITES THEIR ASHES AND ASH LEACHATES AS A FUNCTION OF CONCENTRATION RATIOS

	Lignite		Ash		Ash Leachate	
Concentration Ratio Range[a]	Number of Elements	Percent	Number of Elements	Percent	Number of Elements	Percent
0.5 through 2.0	43	58.9	17	28.8	7	21.2
0.25 through 4.0	57	78.1	44	74.6	14	42.4
0.10 through 10.0	68	93.2	57	96.6	22	66.7
Total samples	73	100.0	59	100.0	33	100.0
Total ratio range	0.02 through 8.0		0.20 through 15		0.002 through 190	

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[a] The ratio reported is the ratio of the Mercer County sample concentration in ppm to the Dunn County samples in ppm. See Table 6 for ratios for individual elements.

results, in Table 3, show wide variability with little similarity between the fraction leachable from the Mercer gasified ash and Dunn laboratory ash.

In examining Table 3, two things are apparent, neither of the samples (Dunn nor Mercer) are dominant in the leach tests *and* the variation in the ratio of the Mercer to Dunn percent leachable is large (0.002 to 190). Only five of the 33 elements common to both samples fall within plus or minus 50 percent of one another (ratio of .5 to 1.5). The variability of the results leads one to postulate, and perhaps conclude, that laboratory prepared ash is not representative of gasifier ash. This result was anticipated by the authors because of the differences in the previous chemical environments (particularly temperature) of the laboratory prepared ash and gasifier ash.

Twenty-four of the 33 elements reported in Table 3 show that Dunn County lignite laboratory prepared ash is more leachable than gasifier ash while nine were less leachable. Consequently, in the majority of cases (73%) the maximum solution rate is given by the laboratory prepared ash. These maximum solution concentrations and their rates are not to be confused with the actual field leachate concentrations and would be expected to be considerably lower than (1/10 to 1/1000 -authors' judgment) the maximum value reported. Furthermore, as time proceeds the actual leach rates and concentrations will decline due to increased compaction of the returned overburden and the progress toward chemical equilibrium between the ash and infiltrated groundwater.

In spite of the above, an estimate of the maximum initial solution rates in pounds per day has been made. The results of this analysis are shown in Tables 4 and 5. These data were generated using Table 3 (columns 1 and 3) and data from Somerville, et al. (1976)[2]. The results of the analysis have been separated into two tables (4 and 5) to show which elements were more leachable from the gasifier ash and which were more leachable from the laboratory prepared ash. The first table, 4, presents the results for the gasifier ash; the second, 5, for the laboratory ash. The results indicate that the sulfur, sodium, calcium, potassium, and iron have the highest potential to enter the groundwater system through the leaching process. The pH of the ash leachates always indicated a basic solution compatible with Fort Union Lignite. All of these elements presently exist in the groundwater of Dunn County.

The similarity of the two coals can be examined by forming the ratio of the concentrations for each element in the lignites, their ashes, and of the percentage leachable in the ashes. These ratios are reported in Table 6. A ratio value of unity means that the same concentration (dry coal basis) exists in both coals. Consequently, many ratio values close to unity imply a basic similarity between the two groups of samples. Examination of Table 6 shows that Mercer and Dunn County lignites are quite similar. This is also borne out by Table 7 which shows that 59 percent of the elements had a ratio value that fell between 0.5 and 2.0. Based upon our experience and others (See Table 10 of Gluskoter et al. (1977)[6]) this level of variability is typical of coals including western coals. On the other hand, examination of the ash and ash leachate columns indicates a general decrease in similarity. This is particularly true of the ash leachates which show only 67 percent of the elements falling within an order of magnitude of one another (ratio range of 0.1 to 10). A similar divergence from the lignite samples, although not as pronounced, can also be observed in the ash samples.

Trace Elements and Environmental Analysis of Groundwater Impact

There are several reasons, why the above data are not well suited to environmental analyses dealing with groundwater impact of mine disposed solids. Some of the principal reasons are:

- The chemistry of the element in the coal, ash, and ash leachate is completely undefined.
- A basic understanding dealing with the chemistry of trace metal components in the geochemical setting is missing.
- The physical system setting is immensely complex; it includes a short term (years), varying, ill-defined geology, particularly during post-mining conditions. Further, the geochemistry varies with depth and topography and the surface experiences a random distribution and water influx (rain).
- The potentially complex chemistry of the

ash when combined with other disposed solids and sludges is not well understood. (e.g., cooling tower blowdown, biotreatment sludges (if any) and water treatment plant sludges).

*The general lack in terms of both quality and quantity of the geological field data required by the sophisticated mathematical models that possess the potential, although presently not the capability, to predict post-mining groundwater chemistry and groundwater impact.

In spite of the above, the data are somewhat useful in determining what elements are likely to not have significant impact from a quantity view point. Additionally, the analyses can narrow considerably the breadth of investigation required to assess the potential impact.

CONCLUSIONS

The data presented indicate that Mercer and Dunn County lignite are basically similar in terms of trace element constituents. Although not entirely conclusive, the same is not true of their ashes and ash leachates. Assuming that their ashes and ash leachates should show the same basic similarity, one has to conclude that the processes the two lignites and their ashes were exposed to are responsible for differences in elemental constituents. Consequently, it is probable that the laboratory ashing procedure (ASTM D 271-68) does not simulate the gasification process well enough to allow use of the laboratory data in environmental analyses.

Further, the quantity and variability of the data reported, as well as the reasons cited above, indicate that use of analytical data of this type in a mathematical model will be difficult, if not impossible. Use of "worst case" experimental biological screening analyses may be the only near term solution to this problem. It is clear that use of trace element analyses alone do not address the groundwater impact question.

RECOMMENDATIONS

The following recommendations are those of the authors and do not necessarily represent the position of either the Engineering Experiment Station or the sponsor.

1. Groundwater monitoring wells should be established in and adjacent to the mine and waste disposal areas. The wells should be sampled and samples analyzed for trace and major inorganic elements and organic compounds.

2. Trace element emissions from a gasification facility should not be regulated until their impact is well understood and adequate and inexpensive instrumentation is developed.

3. Samples of Mercer County lignite should be obtained, ashed under ASTM D 271-68 and leached. Elemental analysis of the ash and its leachate should be completed and compared with the data of this report.

4. A laboratory ashing technique that simulates the Lurgi dry ash gasification environment should be developed.

The first recommendation is obvious, and this would probably be required under existing laws. The second is justified in the authors' view by the following:

*The results of this study indicate that even under "worst case" conditions trace element impact will be minor.

*There have been only scattered instances of negative trace element impact in several decades of successful power plant operation. A gross environmental impact has not been observed.

*The measurement techniques for both trace element determinations and their impacts are still being developed and are expensive and difficult to complete.

*Monitoring of trace element emissions (gaseous, solid, or liquid) would be very difficult to carry out on a continuous basis with existing equipment.

The third recommendation would complete the baseline data missing from this paper. The fourth action is needed to allow prospective developers to make reasonable assessments of the potential impact of disposed gasification ash in the mined area.

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APPENDIX A, ANALYTICAL METHODS USED IN DETERMINING TRACE ELEMENT CONCENTRATIONS IN THE LIGNITE AND ASH SAMPLES

Analytical Methods

Several independent methods were used in the analysis of the samples resulting in some duplication for certain elements. In cases where the survey analysis, Spark Source Mass Spectrometry (SSMS) for a particular element was duplicated by a more precise analysis only the latter results are reported. The methods of analyses utilized were: spark source mass spectrometry, atomic absorption, ion-specific electrode, ultimate analysis and mineral analysis using gravimetric, volumetric, and colorimetric procedures.

SSMS has several advantages for trace element surveys and has become a commonly used analytical tool for the analysis of fossil fuels. SSMS allows the simultaneous determination of approximately 80 elements with typical detection limits for the majority of elements in the order of 50 to 100 parts per billion. An advantage of the spark source mass spectrograph is that it utilizes a small amount of sample. This fact can be a benefit when the samples are limited but is a disadvantage when tonnage quantities are to be represented by a spark source trace element scan. Sample preparation is extremely important in SSMS, but, as in any trace element analysis, large scale samples cannot be accurately represented unless great attention is paid to sample preparation.

The procedure for coal analysis includes reduction of the size of the sample particles to -200 mesh. The gasifier ash leach samples were thermally ashed at 350°C in a quartz boat in a laboratory oven. A portion of the sample was then mixed with an equal weight of high purity compactable graphite. An internal standard, indium, was added along with a few drops of redistilled ethyl alcohol. The mixture was slurried with redistilled alcohol in an agate mortar and pestle. The sample-graphite slurry was dried using infrared lamps. The procedure was then repeated, slurrying and drying, until a homogeneous electrode mixture was assured. The sample-graphite mix was then packed into holes drilled in a specially cleaned polyethylene slug. This slug was then inserted into a metal die and subjected to about 15 to 18 tons of force. The sample-graphite electrodes were then mounted in the machine for sparking.

The mass spectrum produced on the photoplate is a summation of the elemental components of the electrode. The ion intensity of a spectral line is related directly to the concentration of the components at least over a concentration range of 10^5:1. Therefore, by running a series of decreasing exposures, the relative concentration of elements from a major to a trace can be established by knowing the concentration of the internal standard added during sample preparation. Analysis by spark source mass spectrometry will not report elements with concentrations greater than 1,000 parts per million wt. Elements above this amount are reported as major components (MC).

Mineral analyses were performed by procedure listed ASTM D-2795-69, *Gaseous Fuels: Coal and Coke: Atmospheric Analysis, Analysis of Coal and Coke Ash,* part 26, November 1974. Due to the small amount of whole dry coal available for analysis, an additional source of data for the mineral analyses of coal samples from the same mine was sought. A report by the U.S. Bureau of Mines, RI 7158, containing average values from 22 sample locations in the North American Mine at Zap, North Dakota, was used to support, and in some cases supplement, values obtained for the coal sample analyzed in this study (Sondreal et al. 1968)[5]. The following elements were determined in the coal and gasifier ash from the mineral analysis: aluminum, calcium, iron, magnesium, phosphorus, potassium, silicon, sodium, sulfur, and titanium. The concentrations of 14 elements in several of the samples were determined individually by wet chemical methods.

Mercury was determined in all samples by flameless atomic absorption with a double gold amalgamation using the following procedure. The sample was burned in a quartz tube and the mercury was collected on a gold coil. The gold coil was heated and the mercury transferred to a second gold coil. The second gold coil was heated and the mercury passed through a cell in the light path of the atomic absorption spectrometer. The two transfers serve to remove hydrocarbon interferences. The equipment was standardized by injecting known amounts of mercury vapor into the system.

Fluorine was determined in all samples using the USGS method of analysis. The samples were ashed in a slurry of magnesium oxide and magnesium nitrate and then fused with sodium hydroxide. The dissolved fusion was buffered with ammonium citrate, and the fluorine was determined using a fluoride specific-ion-electrode.

Cadmium was determined in all samples via atomic absorption using the following procedure. The samples were put into solution using aqua regia and hydrofluoric acid. They were then stabilized with boric acid and analyzed via atomic absorption versus aqueous standards having the same boric acid content.

Barium and strontium were analyzed for by atomic absorption, using the procedure outlined above, in the dry coal ash and gasifier ash.

Boron was analyzed in the gasifier ash and gasifier ash leach by the following methods. The gasifier ash was washed in sodium carbonate and then fused to obtain a solution followed by a distillation to remove interferences. The solution was then analyzed via a curcumin colorimetric analysis. The gasifier ash leach was run directly with boron determined by the curcumin colorimetric method.

Leaching Method

Since it was suspected that many of the elements found in coal would probably be retained in the gasifier ash, and plans for burial of the ash in the mine area, an experiment was designed to study the leaching characteristics of the coal ash and gasifier ash.

Ten grams of gasifier ash, ground to pass a -60 mesh screen, were slurried with 50 ml of distilled-demineralized water. The solution was refluxed for 16 to 24 h with the temperature held at the boiling point of water. At the conclusion of the refluxing the leachate was analyzed with the following tests performed.

1. Survey Analysis - Spark Source Mass Spectrometry
2. Fluorine - USGS Method Ion-Specific Electrode
3. Mercury - Flameless Atomic Absorption
4. Boron - Atomic Absorption
5. Sodium - Atomic Absorption
6. Strontium - Atomic Absorption
7. Barium - Atomic Absorption
8. Aluminum - Atomic Absorption
9. Calcium - Atomic Absorption
10. Silicon - Atomic Absorption
11. Potassium - Atomic Absorption
12. Cadmium - Atomic Absorption
13. Sulfur - Gravimetric

Table A-1 reports the method used for each of the 73 elements.

TABLE A-1

ELEMENTS CONSIDERED AND ANALYTICAL METHOD USED FOR CALCULATIONS*

Elements	Whole Coal	Gasifier Ash	Ash Leach
1. Ag, silver	NR	SSMS	SSMS
2. Al, aluminum	MA	MA	AA
3. As, arsenic	SSMS	SSMS	SSMS
4. Au, gold	NR	NR	NR
5. B, boron	SSMS	C	C
6. Ba, barium	AA	AA	AA
7. Be, beryllium	SSMS	SSMS	NR
8. Bi, bismuth	NR	NR	NR
9. Br, bromine	SSMS	SSMS	SSMS
10. Ca, calcium	MA	MA	AA
11. Cd, cadmium	AA	AA	AA
12. Ce, cerium	SSMS	SSMS	NR
13. Cl, chlorine	SSMS	SSMS	AA
14. Co, cobalt	SSMS	SSMS	SSMS
15. Cr, chromium	SSMS	SSMS	SSMS
16. Cs, cesium	SSMS	SSMS	SSMS
17. Cu, copper	SSMS	SSMS	SSMS
18. Dy, dysprosium	SSMS	SSMS	NR
19. Er, erbium	NR	SSMS	NR
20. Eu, europium	SSMS	SSMS	NR
21. F, fluorine	IE	IE	IE
22. Fe, iron	MA	MA	SSMS
23. Ga, gallium	SSMS	SSMS	SSMS
24. Gd, gadolinium	SSMS	SSMS	NR
25. Ge, germanium	SSMS	SSMS	SSMS
26. Hf, hafnium	NR	SSMS	NR
27. Hg, mercury	FAA	FAA	FAA
28. Ho, holmium	SSMS	SSMS	NR
29. I, iodine	SSMS	SSMS	SSMS
30. Ir, iridium	NR	NR	NR
31. K, potassium	MA	MA	AA
32. La, lanthanum	SSMS	SSMS	NR
33. Li, lithium	SSMS	SSMS	SSMS
34. Lu, lutetium	NR	SSMS	NR
35. Mg, magnesium	MA	MA	SSMS
36. Mn, manganese	SSMS	SSMS	SSMS
37. Mo, molybdenum	SSMS	SSMS	SSMS
38. Na, sodium	MA	MA	AA
39. Nb, niobium	SSMS	SSMS	NR
40. Nd, neodymium	SSMS	SSMS	NR
41. Ni, nickel	SSMS	SSMS	SSMS
42. Os, osmium	NR	NR	NR
43. P, phosphorus	MA	MA	SSMS
44. Pb, lead	SSMS	SSMS	SSMS
45. Pd, palladium	NR	NR	NR
46. Pr, praseodymium	SSMS	SSMS	NR
47. Pt, platinum	NR	NR	NR
48. Rb, rubidium	SSMS	SSMS	SSMS
49. Re, rhenium	NR	NR	NR

TABLE A-1 (Continued)

Elements	Whole Coal	Gasifier Ash	Ash Leach
50. Rh, rhodium	NR	NR	NR
51. Ru, ruthenium	NR	NR	NR
52. S, sulfur	WC	MA	WC
53. Sb, antimony	SSMS	SSMS	SSMS
54. sc, scandium	SSMS	SSMS	SSMS
55. Se, selenium	SSMS	SSMS	SSMS
56. Si, silicon	MA	MA	AA
57. Sm, samarium	SSMS	SSMS	NR
58. Sn, tin	SSMS	SSMS	SSMS
59. Sr, strontium	AA	AA	AA
60. Ta, tantalum	NR	SSMS	NR
61. Tb, terbium	SSMS	SSMS	NR
62. Te, tellurium	SSMS	SSMS	NR
63. Th, thorium	SSMS	SSMS	NR
64. Ti, titanium	MA	MA	SSMS
65. Tl, thallium	NR	SSMS	NR
66. Tm, thulium	NR	SSMS	NR
67. U, uranium	SSMS	SSMS	NR
68. V, vanadium	SSMS	SSMS	SSMS
69. W, tungsten	NR	SSMS	SSMS
70. Y, yttrium	SSMS	SSMS	SSMS
71. Yb, ytterbium	NR	SSMS	NR
72. Zn, zinc	SSMS	SSMS	SSMS
73. Zr, zirconium	SSMS	SSMS	NR

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* Analytical procedure used, meaning of symbols:

C - curcumin colorimetric analysis
AA - atomic absorption versus aqueous standards
IE - ion-selective electrode
MA - standard mineral analysis, ASTM D2795-69
NR - not reported
WC - wet chemical or gravimetric
FAA - flameless atomic absorption
SSMS - spark source mass spectrometry, detection limit considered <0.1 ppm

COMBINED-CYCLE POWER SYSTEMS BURNING LOW-BTU GAS

F. L. Robson* and W. A. Blecher**
United Technologies Research Center
East Hartford, Connecticut

Abstract

Future power systems will be required to burn coal in an environmentally acceptable manner. One of the most attractive advanced technology power systems is the combined gas turbine and steam turbine system, the combined cycle, which offers higher efficiency and lower capital costs than the more conventional steam system. These advantages will enable the combined-cycle system to be used in conjunction with expensive fuel treatment processes such as gasification and subsequent pollutant cleanup resulting in reduced emissions while producing electrical power at costs projected to be significantly less than conventional coal-fired steam plants with stack gas cleanup.

Decriptions of the gasification process, fuel gas cleanup and power systems are given with pertinent characteristics. The estimated emissions of the various systems are tabulated and the costs of the integrated gasification/power plant are compared with those for a conventional steam plant with stack gas cleanup.

INTRODUCTION

One of the major energy goals set by the present Carter Administration is that of increased use of coal in industrial and utility applications. Historically, coal usage has been increasing slowly, < 3 percent/yr, and by 1985 would reach approximately 800 million ton/year (Figure 1). By emphasizing the use of coal, it is projected that 1.1 billion tons/yr could be used. While it is not clear that this goal can be achieved, the utility industry has indicated that it will meet its obligations by increasing the demand for coal from 430 million tons/yr to 790 million tons/yr in 1985.

This increased use of coal must be done in an environmentally acceptable manner and, thus, between now and 1985, emphasis will be placed upon low-sulfur western coals and upon flue gas desulfurization. In the years beyond 1985, it is hoped that more efficient and less costly coal-burning power systems having lower emissions of SO_2 and NO_x will become commercially feasible. One of the most attractive of these advanced power systems is the combined gas turbine and steam turbine system (combined cycle) used in conjunctin with coal gasification and fuel gas cleanup which produce clean low-Btu gases, i.e., gases having heating values on the order of 1150 kcal/m^3 (1,000 kcal/kg, 130 Btu/ft^3).

To achieve the potential savings in capital and in fuel use, the power system and the fuel processing system must be closely integrated such as shown in Figure 2. In this power plant, air from the gas turbine is used in the coal gasifier while steam generated by cooling the hot fuel gas is used in the power system. Other configurations are possible including the use of oxygen rather than air in the gasifier and the use of a variety of cleanup systems.

During the past several years, under EPA auspices, United Technologies Research Center, in conjunction with Foster Wheeler Energy Corp., Fluor Engineers and Constructors and Hittman Associates, Inc., have investigated the technical, economic, and emission characteristics of power plants based upon a number of gasifier types with both low- and high-temperature sulfur cleanup systems and advanced technology combined-cycle systems. The current paper will describe only a two-stage, entrained-flow gasifier with both low-temperature and high-temperature sulfur cleanup used with a combined-cycle system having a 1425° C (2600° F) gas turbine.

POWER SYSTEM

The power system is of nominal 1000-MW size and consists of 4 advanced gas turbines generating a total of 720 MW and a conventional heat recovery steam system generating

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* *Chief, Utility Power Systems*

** *Senior Research Engineer*

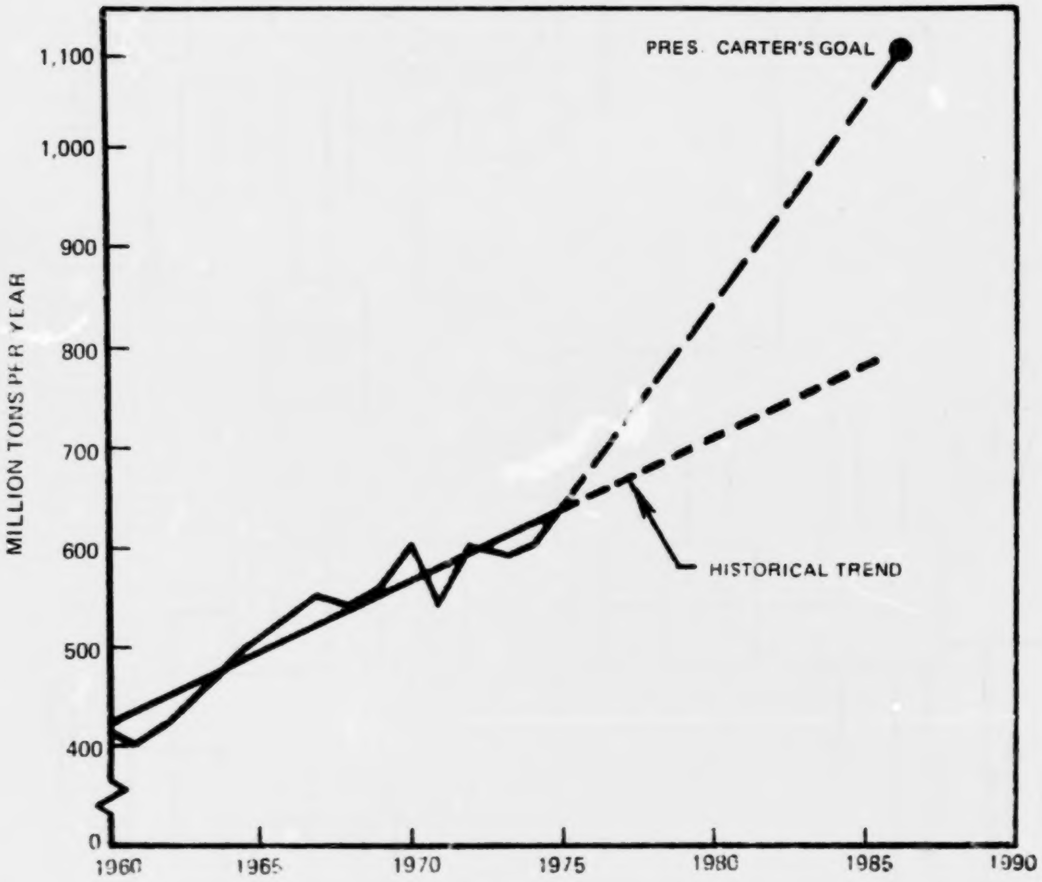

Figure 1. U.S. bituminous coal production.

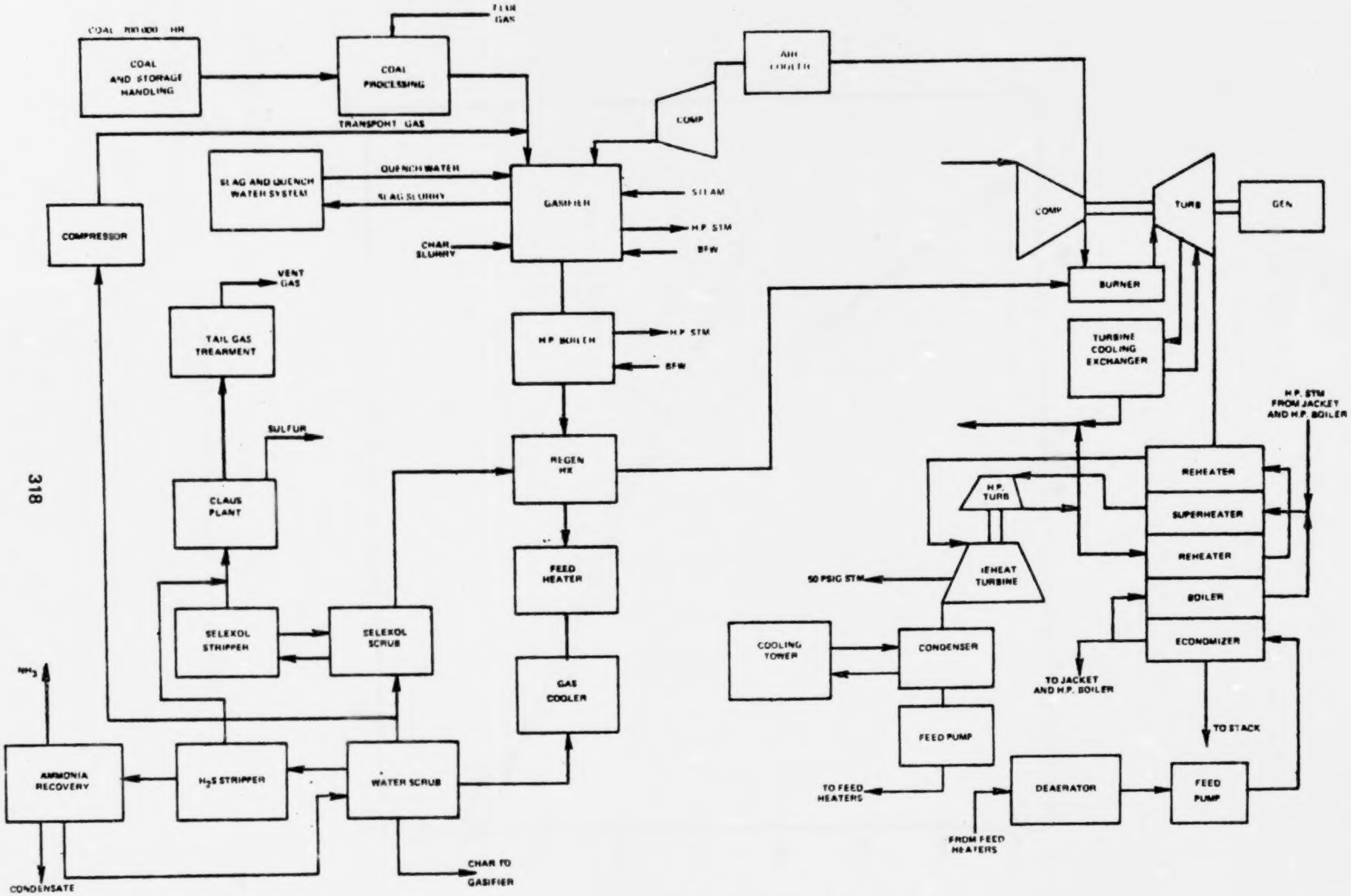
COAL HR
COAL AND STORAGE HANDLING
COAL PROCESSING
FLUE GAS
TRANSPORT GAS
AIR COOLER
COMP
SLAG AND QUENCH WATER SYSTEM
QUENCH WATER
SLAG SLURRY
GASIFIER
STEAM
H.P. STM
BFW
CHAR SLURRY
COMPRESSOR
VENT GAS
TAIL GAS TREAMENT
H.P. BOILER
H.P. STM
BFW
SULFUR
CLAUS PLANT
REGEN HX
FEED HEATER
SELEXOL STRIPPER
SELEXOL SCRUB
GAS COOLER
NH3
AMMONIA RECOVERY
H2S STRIPPER
WATER SCRUB
CONDENSATE
CHAR TO GASIFIER
COMP
TURB
GEN
BURNER
TURBINE COOLING EXCHANGER
H.P. STM FROM JACKET AND H.P. BOILER
REHEATER
SUPERHEATER
REHEATER
BOILER
ECONOMIZER
H.P. TURB
REHEAT TURBINE
50 PSIG STM
COOLING TOWER
CONDENSER
FEED PUMP
TO JACKET AND H.P. BOILER
TO STACK
TO FEED HEATERS
DEAERATOR
FEED PUMP
FROM FEED HEATERS

Figure 2. Air-blown BCR/Selexol

445 MW. The net output power (using low-temperature cleanup) is 1088 MW and the estimated overall efficiency, coal pile-to-busbar is 43.7 percent.

Gas Turbine

A number of studies (1,2,3) have indicated that the gas turbine portion of the combined-cycle system in the integrated coal gasification/power station must operate at temperatures of approximately 1325° C (2400° F) or above in order to achieve attractive overall efficiencies or heat rates. Prior UTRC work (3,4) has been based upon turbines of 1425° C turbine inlet with relatively high pressure ratios, e.g., 24:1. These turbines were assumed to have ceramic stators and other static structure requiring essentially no cooling combined with air-cooled rotating blades. While this projected use of ceramics results in attractive performance, a number of problems have been identified (5) and it is perhaps more realistic to identify a cooling scheme for the stators and other static structures which would require less development effort and which could be used in commercial service in the 1980's.

Current commercial engines operate in the 1000° C to 1100° C range with air-cooled stators and blades. However, when an air-blown gasifier is used, some 15-17 percent of the compressor discharge air is diverted to the gasifier and is unavailable for turbine cooling or combustion dilution. Thus, the use of another coolant medium such as water becomes advantageous. The gas turbine used in the present study is based upon advanced versions of large industrial turbines such as the prototype 100-MW UTC/Stal Laval FT50/GT200 (Figure 3), but using water-cooled static structures with air-cooled blades.

The major modification of the gas turbine resulting from the use of low-Btu fuel gas occurs in the combustor section. Because of the smaller amount of air available for cooling in systems using air-blown gasifiers, the combustor design must be one that minimizes the surface to volume ratio since this requires less coolant. The configuration which best fulfills the various requirements is the annular burner which resembles two concentric barrels surrounding the gas turbine between the compressor discharge and the turbine inlet (Figure 4).

A second combustor modification occurs in the fuel injector. Normal practice would have a single injector or perhaps several small injectors for each burner can. Because of the higher volume flow rate required for the low-Btu gas, much larger injector areas are necessary. Tests carried out by UTC and Texaco (6,7) have indicated that a premix injector, one in which the fuel gas and air are intimately mixed prior to combustion, would significantly lower the production of NO_x while lowering the peak temperatures within the burner can. Such a configuration is shown in Figure 4. The emissions characteristics of this combustor will be discussed in a later section.

Steam System

The steam system operates at conventional levels, i.e., 163 atm/510° C /510° C (2400 psi/950° F /950° F). While it would be possible to operate at throttle temperature of 535° C (1000° F), trade-off studies between heat exchanger size and materials versus small increases in performance indicate the lower temperature system would result in lower costs of electricity.

FUEL PROCESSING SYSTEM

The fuel processing system consisting of the coal gasifiers and the fuel gas cleanup system processes 317,460 kg/hr (700,000 lb/hr) of Illinois No. 6 coal into a clean fuel gas having a heating value of 1,584 kcal/m^3 (178 Btu/ft^3).

Although there is a wide variety of coal gasification processes currently under study, e.g., fixed-bed, entrained-flow, fluid-bed, and molten-bed, the present paper will emphasize only the entrained-flow gasifier. In particular, a two-stage gasifier based upon the Bituminous Coal Research, Inc., (BCR) BiGas design, but modified for air-blown fuel gas production by Foster Wheeler Energy Co., will be discussed.

Similarly, a number of low-temperature sulfur removal systems are commercially available which could be applied to the cleaning of fuel gas at low temperatures(3) i.e., < 120° C (250° F). However, only the Selexol physical

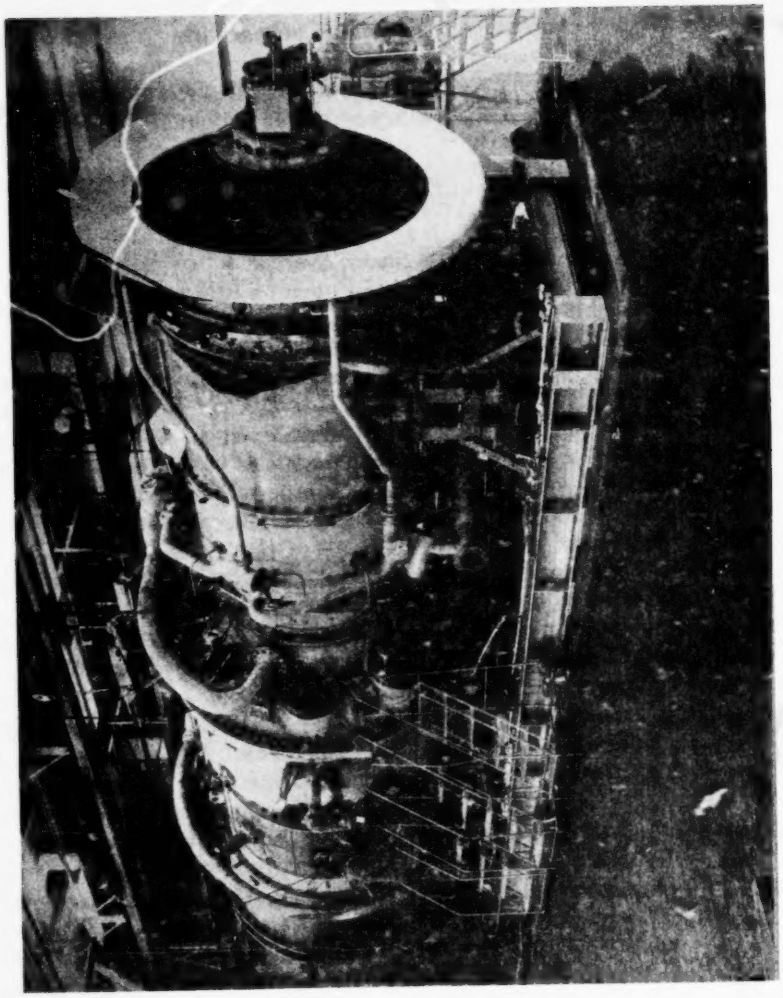

Figure 3. FT50 gas turbine.

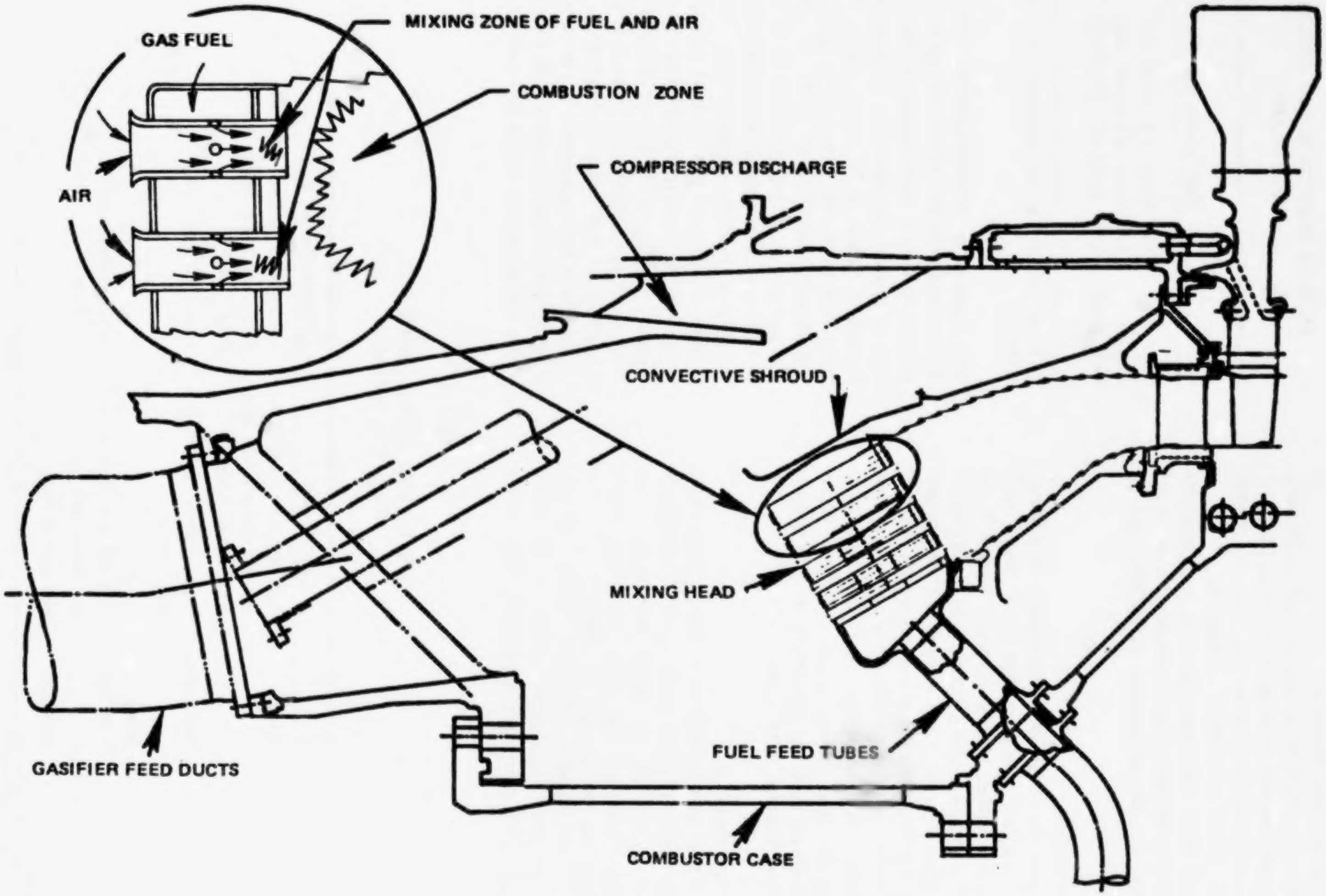
GAS FUEL
MIXING ZONE OF FUEL AND AIR
COMBUSTION ZONE
AIR
COMPRESSOR DISCHARGE
CONVECTIVE SHROUD
MIXING HEAD
FUEL FEED TUBES
GASIFIER FEED DUCTS
COMBUSTOR CASE

Figure 4. Potential pre-mix combustor layout.

absorbent process of the Allied Chemical Corporation will be discussed.

Although high-temperature sulfur cleanup processes are still in the laboratory-scale stage, they are potentially attractive from an overall power plant efficiency viewpoint. Thus, a calcium carbonate-based process developed by the Consolidation Coal Company, division of Continental Oil Corporation (CONOCO) will be described.

Coal Gasifier

A schematic of the two-stage, entrained-flow gasifier including the flow rates and operating parameters is given in Figure 5. In order to increase the efficiency of the system, the steam-to-coal ratio should be minimized since the energy in the steam consumed during gasification cannot be effectively recovered. A reduction in the steam consumption also enhances the performance of the high-temperature cleanup system as will be shown in a later section of this paper.

Fuel Gas Cleanup

The fuel gas coming from the gasifier must be cleaned not only to meet the EPA standards (Table 1), but also to meet restrictions set by the gas turbine. The latter are often more stringent as can be seen in Table 2.

TABLE 1

EMISSION STANDARDS FOR COAL-FIRED POWER PLANTS

	Conventional Plant	Proposed gas turbines*
SO_2	0.57 kg/GJ (1.2 lb/10^6 Btu)	100 ppm
NO_x	0.33 kg/GJ (0.7 lb/10^6 Btu)	75 ppm
Particulates	0.047 kg/GJ (0.1 lb/10^6 Btu)	NA

* For all fuels and at ISO conditions with 15% O_2 in exhaust

Low-Temperature Cleanup - Many of the commercially available cleanup systems operate with comparable removal efficiencies and operating characteristics. The Selexol system selected for discussion uses a physical solvent having a high degree of selectivity for H_2S. A typical configuration for H_2S removal is shown in Figure 6. In those cases where the combination of coal and gasifier type results in significant quantities of COS, or when that component must be scrubbed to a low level, the solvent flow rate must be increased and a flash tank must be added along with a compressor to recycle the flashed gas to the absorber. While this increased flow minimizes the amount of CO_2 in the Selexol stripper off-gas, thereby benefiting the sulfur recover system, it adds to cost and utility requirements.

The absorber is generally run at temperatures slightly lower than ambient and, thus, requires some refrigeration. While this results in an in-

TABLE 2

GAS TURBINE REQUIREMENTS FOR FUEL GAS CLEANUP

	Low-Btu Gas	Typical Current Spec
Sulfur	0.05 Mol % or Less Than Amount to Form 0.6 ppm Alkali Metal Sulfate	$<$ 1.0 Mol % or Less Than Amount to Form 5 ppm Alkali Metal Sulfate
Particulates	4 ppm Weight or 0.0012 gr/ft^3 $> 2\mu$	30 ppm or 0.01 gr/ft^3
Metals		
Vanadium	$<$ 0.003 ppm Weight See Sulfur Spec	$<$ 0.02 ppm Weight $<$ 0.6 ppm
Nitrogen	500 ppm as NH_3	

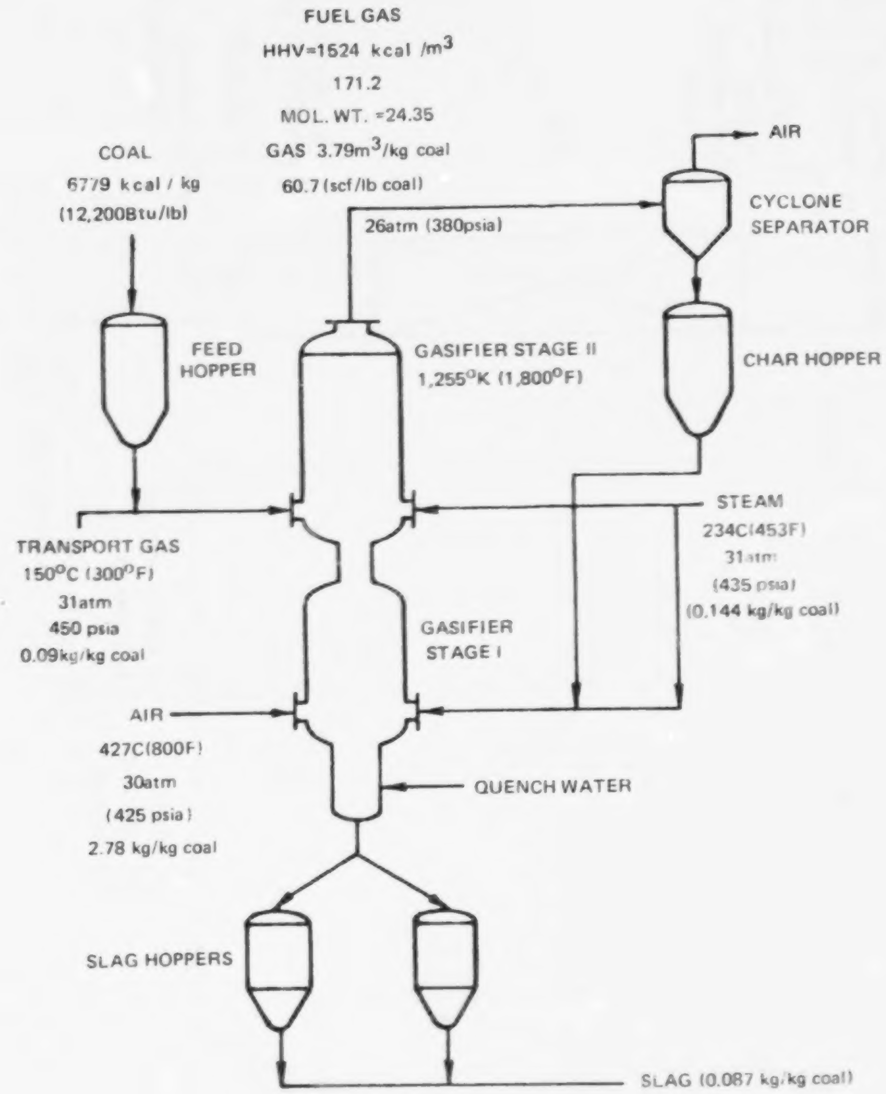
FUEL GAS
HHV=1524 kcal /m^3
171.2
MOL. WT. =24.35
GAS 3.79m^3/kg coal
60.7 (scf/lb coal)
AIR
COAL
6779 kcal / kg
(12,200Btu/lb)
CYCLONE SEPARATOR
26atm (380psia)
FEED HOPPER
GASIFIER STAGE II
1,255°K (1,800°F)
CHAR HOPPER
STEAM
234C(453F)
31atm
(435 psia)
(0.144 kg/kg coal)
TRANSPORT GAS
150°C (300°F)
31atm
450 psia
0.09kg/kg coal
GASIFIER STAGE I
AIR
427C(800F)
30atm
(425 psia)
2.78 kg/kg coal
QUENCH WATER
SLAG HOPPERS
SLAG (0.087 kg/kg coal)

Figure 5. BCR entrained flow gasifier.

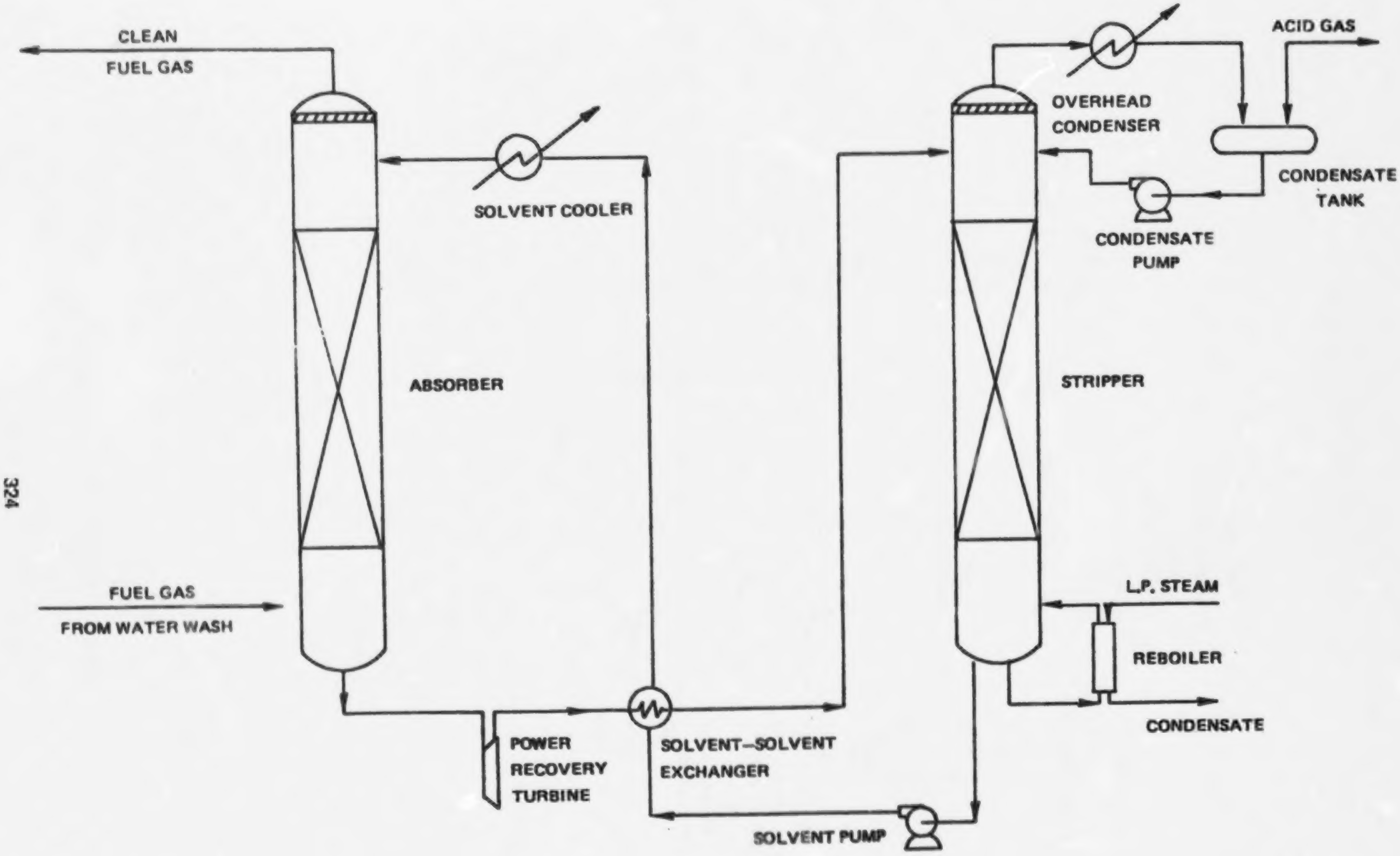
CLEAN
FUEL GAS
SOLVENT COOLER
ABSORBER
FUEL GAS
FROM WATER WASH
POWER
RECOVERY
TURBINE
SOLVENT–SOLVENT
EXCHANGER
SOLVENT PUMP
OVERHEAD
CONDENSER
ACID GAS
CONDENSATE
TANK
CONDENSATE
PUMP
STRIPPER
L.P. STEAM
REBOILER
CONDENSATE

Figure 6. Selexol low-temperature desulfurization.

crease in power consumption over ambient absorber temperatures, solvent flow rate and therefore steam consumption and capital cost are less. The effect of operating temperature on utilities and cost is given in Table 3 for two different fuel gas compositions, one with a low COS concentration requiring only an H_2S-COS based design and the other with a significant amount of COS requiring a COS-based design. In each case, the differences clearly indicate that low-temperature operation is preferable.

For a Selexol desulfurization system operating with the BCR gasifier, a comparison of COS- and H_2S-based designs is given in Table 4. Both designs would result in emissions significantly less than current EPA regulations. The comparison in Table 4 gives an indication of the cost associated with the removal of sulfur to relatively low levels.

High-Temperature Cleanup - The high-temperature cleanup systems offer the advantage of providing a hot fuel gas directly to the gas turbine, thereby utilizing the fuel gas sensible heat in the topping cycle without the need for costly regenerative heat exchangers and without the losses associated with the heat exchange processes. As an example of one of the more attractive processes, the Conoco half-calcined dolomite process was selected for discussion. The desulfurizer operates at temperatures in the 850-900° C range. Both H_2S and COS react with the $CaCO_3$ component of the dolomite in a fluidized bed according to the following reactions:

TABLE 3

LOW VS. AMBIENT-TEMPERATURE SELEXOL OPERATION

	Ambient-Temperature	Low-Temperature	Δ
Equipment Designed for H_2S Removal			
Steam - kg/hr	114,545	48,273	66,272
Net Power - kW	4,270	17,400	13,000
Cost - $\$10^6$	26	16	10
Equipment Designed For COS Removal			
Steam - kg/hr	345,454	138,636	206,818
Net Power - kW	25,530	38,940	13,400
Cost - $\$10^6$	72.6	47	25.6

NOTE: This data should not be used to compare H_2S vs COS removal.

TABLE 4

COMPARISON OF H_2S AND COS BASED DESIGNS

BCR-TYPE GASIFIER-SELEXOL CLEANUP PROCESS

	H_2S-Based Design	COS-Based Design
H_2S in clean gas-ppm	38	13
COS in clean gas-ppm	447	52
Emissions $KgSO_2/GJ$	0.186	0.0252
Power - kW	20,400	39,500
Steam - kg/hr	59,773	153,500
Cost - $\$10^6$	26.3	53.8

Based on coal feed rate of 317,460 kg/hr and low-temperature absorbent.

$$(CaCO_3 \cdot MgO) + H_2S \rightarrow (CaS \cdot MgO) + H_2O + CO_2 \quad (1)$$

$$(CaCo_3 \cdot MgO) + COS \rightarrow (CaS \cdot MgO) + 2\ CO_2 \quad (2)$$

Regeneration of the sulfided acceptor is accomplished in a fluidized reactor at 700° C using a stream of carbon dioxide and water vapor. Makeup dolomite is supplied at 2 percent of the recirculation rate. A schematic of the process is shown in Figure 7. It includes a liquid-phase Claus plant as well as a converter for the spent dolomite.

The desulfurizer reactions are reported to be virtually at equilibrium and performance improves with increased temperature and decreased concentration of the reaction products, CO_2 and H_2O. Temperature is limited by CO_2 partial pressure which must be high enough to prevent calcination of the acceptor. For the BCR gasifier, desulfurization performance at two possible operating conditions is shown in Table 5. The primary difference between the two cases is the steam-to-coal ratio. At the lower ratio, oxidant feed is re-

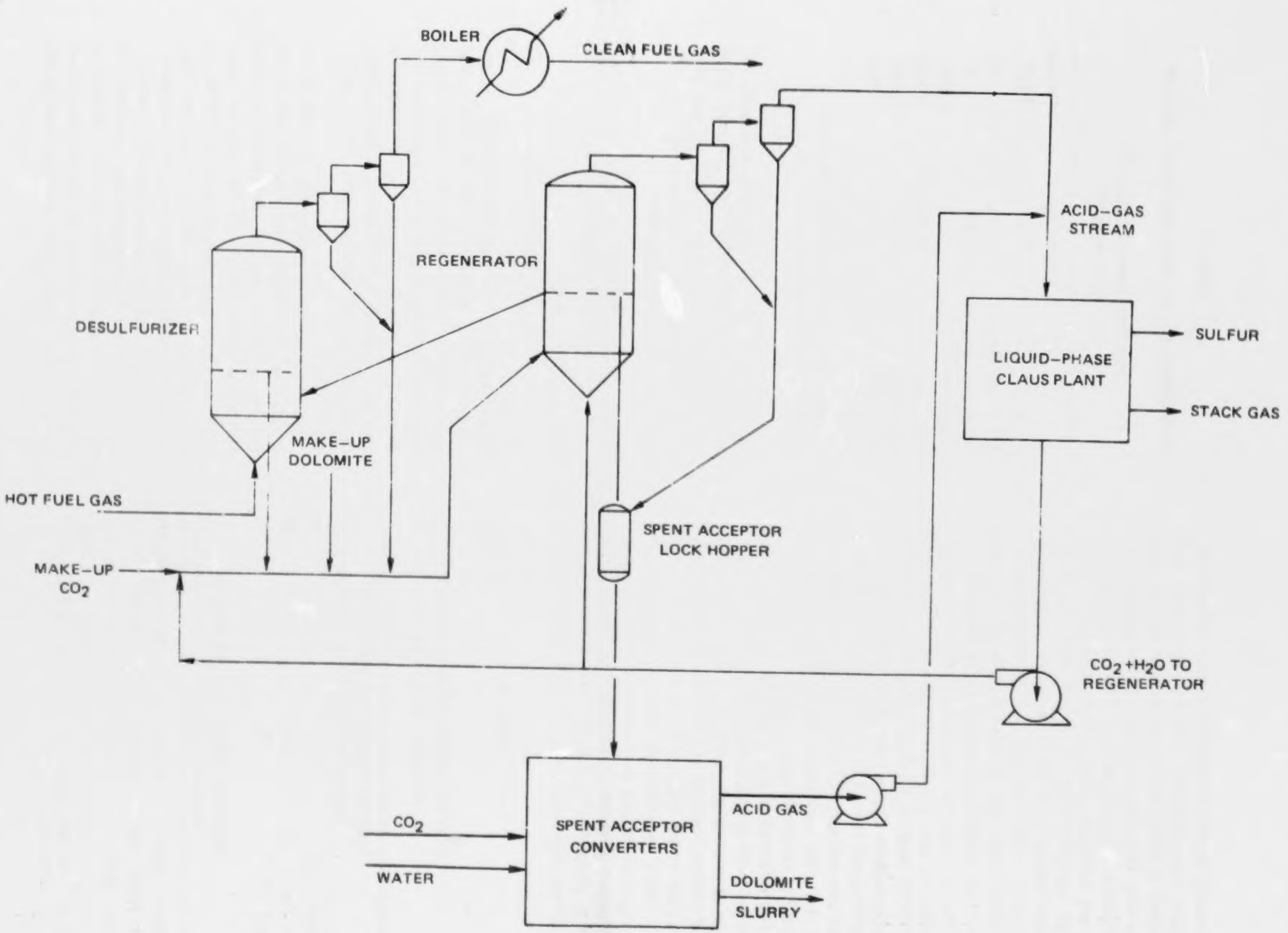
BOILER
CLEAN FUEL GAS
REGENERATOR
DESULFURIZER
ACID–GAS STREAM
LIQUID–PHASE CLAUS PLANT
SULFUR
STACK GAS
MAKE–UP DOLOMITE
HOT FUEL GAS
SPENT ACCEPTOR LOCK HOPPER
MAKE–UP CO_2
CO_2 + H_2O TO REGENERATOR
SPENT ACCEPTOR CONVERTERS
ACID GAS
CO_2
WATER
DOLOMITE SLURRY

Figure 7. Conoco high-temperature desulfurization.

TABLE 5

EFFECT OF STEAM/COAL RATIO ON CONOCO DESULFURIZATION

	High Steam/Coal Ratio		Low Steam/Coal Ratio	
	Desulfurizer In	Desulfurizer Out	Desulfurizer In	Desulfurizer Out
CH_4-Mol/hr	5099.5	5099.5	3775.0	3775.0
H_2	18538.8	19270.9	15314.9	15894.5
CO	25582.2	24851.3	32189.6	31610.0
CO_2	11669.7	13289.7	3396.1	4863.4
H_2S	685.7	68.7	751.0	9.5
COS	143.5	8.6	75.6	2.5
NH_3	609.0	609.0	478.8	478.8
N_2	65634.5	65634.5	53753.3	57353.3
H_2O	14338.1	14222.4	2212.6	2374.5
	142301.0	143054.5	111946.9	112762.5
Steam/Coal Ratio	.567	.144		
Desulfurizer Temperature - C	.927	815		
Sulfur as SO_2 - kg/GJ	.27	.042		

duced to maintain a fixed gasifier temperature and both CO_2 and H_2O concentrations are quite low. The net result is a marked reduction in both. H_2S and COS concentrations in the clean gas. Fortunately, reduced steam feed rates have a favorable effect on both power conversion efficiency and sulfur removal.

Because the fuel gas would not be cooled, a water wash for the removal of ammonia and particulates is not feasible. Therefore, other provisions for handling these constituents must be made. In the case of particulate matter, the sensitivity of turbine materials and coatings dictates a very high degree of removal. Thus, the use of high-temperature desulfurization is contingent on the development of a high-temperature and high efficiency particulate removal device. Such a device will undoubtedly be used in conjunction with conventional cyclones as a "final filter." Several filtration type devices are under development using various concepts such as a porous metal or a sand bed.(5)

Ammonia presents a somewhat different problem in that it can either be removed prior to being burned in the gas turbine or it may be possible to modify the combustor to provide an environment where it will be decomposed to N_2 and H_2. Conventional burners will convert as much as 80 percent of the NH_3 to NO which makes some type of removal system or combustor modification necessary.(3)

EMISSIONS

The emisions from the integrated gasification combined-cycle offer the potential to be significantly lower than those from conventional steam systems with FGD.

Sulfur Oxides

Previous discussion has indicated that the amount of fuel sulfur compounds (H_2S and COS) removed during cleanup is a function of several variables such as type of cleanup, operating temperature, etc. However, no matter which cleanup system is used, the emissions of SO_2 are well below the current regulation for coal-fired steam system (See Figure 8) and below the levels usually removed during flue gas desulfurization.

On the basis of emissions per unit of output (kg/kWhr), the integrated gasification/

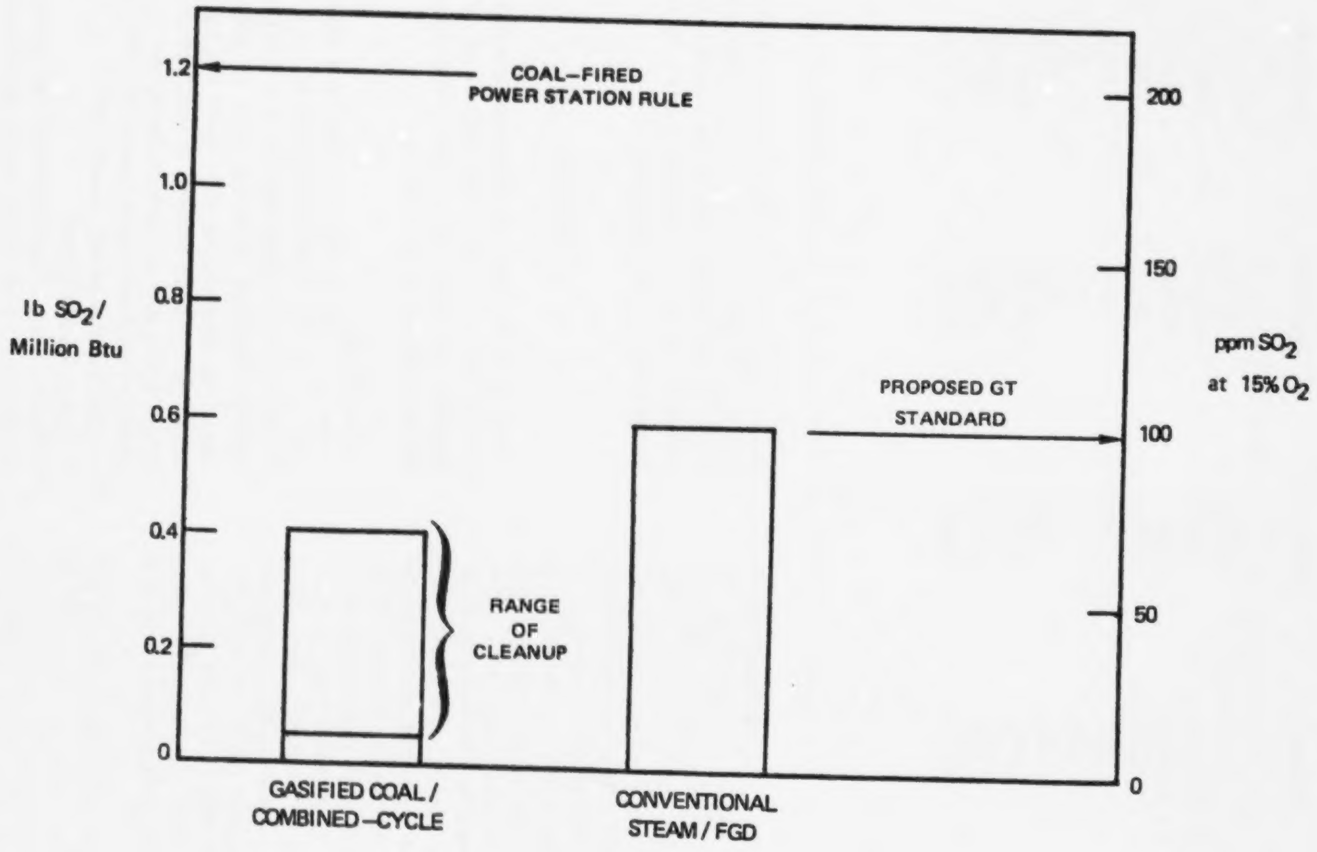

Figure 8. SO_2 emissions.

combined-cycle system would emit between 2.1 and 13.7 × 10^{-4} kg/kWhr versus 27.5 × 10^{-4} kg/kWhr for conventional steam with a 90 percent effective FGD system.

Nitrogen Oxides

The formation of nitrogen oxides results from two sources; thermal NO_x from the oxidation of atmospheric nitrogen at high temperature during combustion, and NO_x from the oxidation of nitrogen compounds in the fuel. Thermal NO_x can be controlled by combustors such as that previously described. Estimates of emissions of thermal NO_x are given in Figure 9.

Unfortunately, it is difficult to estimate the NO_x which could result from fuel-bound nitrogen in low-heating value fuel gases. The amount of nitrogen compounds, usually expressed in terms of ammonia, vary as a function of gasifier type and operating temperature. It is possible to remove a very large fraction of any ammonia in the fuel gas by water wash and in the H_2S removal system which may have some affinity for fuel-bound nitrogen compounds. Thus, with low-temperature systems it is possible to remove the major portion of the nitrogen prior to combustion.

Some consideration has been given to combustor modifications(9) which might be made to reduce the emissions due to fuel-bound nitrogen. At this time, this type of combustor modification would appear to result in combustor configurations which would not be practical for use in advanced combined-cycle systems.

COST OF ELECTRICITY

Overall generating costs are affected primarily by capital and fuel costs and by performance. In the case of low-Btu gasified coal power systems, performance affects the capital cost as well as the fuel cost contribution to overall cost. For a fixed coal feed rate, improved performance means that the capital cost of the fuel processing section can be spread over a greater number of installed kilowatts. As mentioned earlier, continued analyses and small-scale experimentation have led to reduced estimates for steam feed rates to the gasifier. The effect of a reduced steam-to-coal feed ratio and reevaluation of the transport gas requirements are shown in Table 6. The net improvement in gasifier performance is on the order of 6 percent. As an additional benefit, the heat previously required to raise gasifier steam would now be utilized in the power system.

The busbar generating efficiencies of the overall systems are estimated to be 43.7 percent for the low- and 45 percent for the high-temperature cleanup system. Table 7 gives the net power produced, capital cost, and generating costs for the two systems. The costs are based on previous studies(3,4) and are currently being updated. However, it presently appears that there should be little difference. This comparison of high- and low-temperature cleanup shows a lesser difference than did earlier studies. The improvement in gasifier performance, especially the reduced quantity of water vapor in the fuel gas, results in a marked increase in the low-temperature system performance. The high-temperature system, which

TABLE 6

EFFECT OF STEAM/COAL RATIO

Component	High Steam Feed Rate Mol%	Low Steam Feed Rate Mol%
CH_4	3.65	3.37
H_2	12.88	13.68
CO	18.38	28.75
CO_2	8.26	3.03
H_2S	0.48	0.67
COS	0.10	0.07
N_2	46.04	48.02
NH_3	0.4	0.43
H_2O	9.81	1.98
Other Characteristics		
HHV-kCal/m^3	1228	1524
Air/ Coal Ratio	3.09	2.78
Steam/ Coal Ratio	.567	.144
Transport gas/ Coal Ratio	.426	.088
Cold Gas Eff.	78.5%	83%

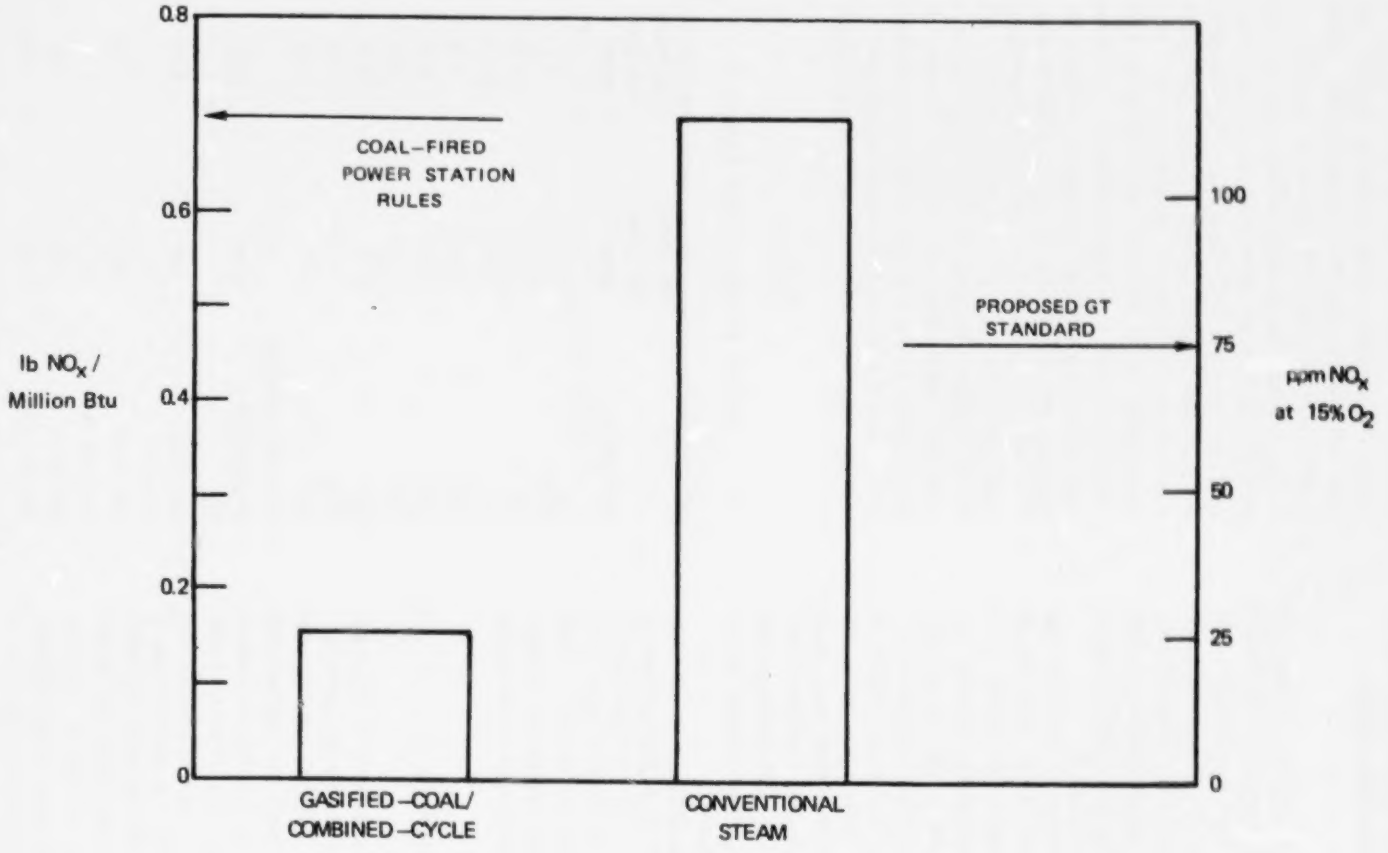

Figure 9. NO_x emissions.

does not require cooling and reheating of the fuel gas, does not benefit from the reduced steam feed rate to the same extent.

The costs for the steam station are those associated with a twin 500-MW station (957-MW net output) with limestone FGD. The cost of power shown in Table 7 is approximately 15 percent higher than for the integrated gasification/combined-cycle systems.

The potential attractiveness of the relatively simple fuel processing section and the somewhat lower generating costs associated with the high-temperature process are predicated on the availability of a high-temperature particulate removal device and also on a gasification system that will produce low levels of ammonia in the fuel gas. It is hoped that efforts will continue in those areas.

SUMMARY

The integration of the combined-cycle power generating system with a pressurized air-blown gasifier makes it possible to economically remove sulfur compounds prior to combustion. The majority of the sulfur in the fuel gas appears as H_2S at a relatively high partial pressure, thus making possible the use of physical as well as chemical sorbents.

In addition to being at pressure, the total gas flow rate through the desulfurization process is reduced by more than a factor of two when compared to the flue gases from a coal-fired boiler. Thus, for a gas turbine cycle having a pressure ratio of 16:1, the cleanup system volumetric flow rate is reduced by over 32:1 when compared to a flue gas desulfurization system.

As a result of the high-pressure operation, high removal efficiency is possible. Also, most processes produce an acid gas stream that is rich in H_2S thereby providing an excellent feed to a Claus sulfur recovery plant.

The capital costs associated with sulfur cleanup also appear to favor the integrated system. For example, estimates of the fuel gas cleanup and sulfur recovery system costs show that for a removal effectiveness of approximately 94 percent, the associated cost per lb/hr of S removed is $1075; for over 99-percent removal, the cost is $2070. In comparison, the costs for 90 percent effective flue gas desulfurization systems are $2600 lb/hr of S for limestone slurry(10) and $10,000 lb/hr of S for citrate(11) systems. None of the foregoing include credit for sulfur recovery or costs for offsite waste disposal.

While sulfur removal costs do not tell the whole story, they are indicative of overall power costs; e.g., estimates of busbar costs for the advanced combined-cycle systems(4,12)

TABLE 7

PERFORMANCE AND COST SUMMARY

	BCR-Selexol Low-Temp	BCR-Conoco High-Temp	Conventional Steam FGD
Gasifier & Cleanup System Cost - $	231,300,000	210,800,000	94,000,000
Power System Cost - $	285,300,000	296,500,000	415,400,000
Total Cost - $	516,600,000	507,300,000	509,400,000
Net Plant Output - MW	1088	1126	957
Overall Plant Efficiency - %	43.5	45.0	36.5
Generating Costs - mills/kwh			
Owning Costs	13.2	12.5	14.7
Operation and Maintenance	4.4	4.1	4.0
Fuel ($1.00/MMBtu)	7.8	7.6	9.6
Total Generating Cost - mills/kwh	25.4	24.2	28.3

are as much as 15 percent lower than that of a conventional steam plant with limestone FGD.

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CROSS-MEDIA ENVIRONMENTAL IMPACTS OF COAL-TO-ELECTRIC ENERGY SYSTEMS

Edward S. Rubin
Cary N. Bloyd
Paul J. Grogan
Francis Clay McMichael

Department of Engineering
and Public Policy
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Abstract

The types and rates of pollutant emissions from coal utilization systems depend on process design, coal characteristics, and environmental control technology. The latter is strongly influenced by environmental regulatory policy which has historically focused on pollutant emissions to a single environmental medium (air, land, or water) without rigorous analysis of the energy and secondary environmental impacts that follow. It thus remains unclear as to whether regulations requiring stringent control of single pollutants in a single medium may actually be counterproductive to overall environmental quality when energy and cross-media impacts are considered. The present paper describes an approach being developed at Carnegie-Mellon University to systematically address such issues in the context of conventional and advanced technologies producing electricity from coal. Analytical models are described which compute system residuals to air, land, and water as a function of coal parameters and system design after all ancillary energy penalties are accounted for. Included are models of a coal cleaning plant, flue gas desulfurization system, dry particulate collector, wastewater control system, and low-Btu gasification plant coupled to either a conventional or combined cycle power generation system. Application of these models is illustrated in the context of alternative regulatory strategies for sulfur dioxide emission control. Methodologies for assessing cross-media tradeoffs in the context of societal value judgments are also discussed.

INTRODUCTION

Increasing interest in the use of coal as an energy source has sharpened our awareness of the close relationship between energy technology development and environmental regulatory policy. Environmental regulations limiting gaseous and liquid discharges from coal utilization systems can have significant ramifications on the cost and feasibility of specific processes. At the same time, adequate environmental control is imperative if the adverse effects of coal utilization are to be mitigated. The goal of informed public policy is to develop regulations and standards that provide acceptable environmental protection in a way that is equitable to competing energy processes. This requires that environmental regulatory policy be sensitive to adverse effects in all environmental media (air, land, and water), and that it also be sensitive to the impact specific regulations can have on the viability of alternative coal technologies. Both concerns suggest the need for a comprehensive "systems" view of the environmental impacts of coal conversion technologies. This paper describes the status of work at Carnegie-Mellon University to develop such a model for coal-to-electric systems, including advanced coal conversion processes. Results are presented following a review of current regulatory policy for coal conversion technologies.

REVIEW OF CURRENT REGULATORY POLICY

A 1975 paper by Rubin and McMichael(1) summarized the nature and status of regulations and standards affecting coal utilization processes. For air and water pollutants two types of standards exist: standards of ambient environmental quality, and standards limiting source emissions. For air, environmental quality standards include national primary and secondary ambient air levels designed to protect human health and welfare. Special standards also prevent the significant deterioration of superior air quality. For water, environmental quality standards are similarly designed to protect human health and welfare as well as aquatic species in streams and rivers. While ambient air quality standards apply uniformly across the nation (except where state and local standards are more stringent), ambient water standards vary markedly from stream to stream. They are set principally by state and local agencies subject to federal approval. Uniform standards for drinking water, however, now apply nationally.

Discharge standards for air and water pollutants are the principal enforcement tool for achieving standards of environmental quality. Existing sources are regulated by state and local agencies. New sources of certain industrial categories are regulated federally via New Source Performance Standards (NSPS) promulgated by the U.S. Environmental Protection Agency (EPA). These require the use of Best Available Control Technology (BACT) for specified air and/or water pollutants. For most processes, they pose an important design constraint which adds to the cost of technology.

At the present time, no NSPS regulations exist for synfuel processes, though regulation of process sulfur emissions from Lurgi hi-Btu gasification plants is being considered by EPA.(2) Table 1 summarizes the air and water pollutants currently regulated by NSPS for coal-fired steam-electric generators, petroleum refineries and by-product coke plants. The latter two may be suggestive of future coal refineries producing synthetic gas or liquid from coal. Regulation of solid waste effluents from coal utilization systems is currently subject to state and local standards only. Federal regulations in the solid waste area is limited to special situations such as mining and ocean dumping, although increased regulation is likely as a result of the 1976 Solid Waste Recovery Act.

Multimedia Impact of NSPS Regulations

The choice of technology and the energy penalty incurred in meeting New Source Performance Standards gives rise to what we call "cross-media" environmental impacts. This refers to situations in which the reduction of a pollutant emission to one environmental medium (air, land, or water) increases the pollutant burdens in other media. Some examples of this are well known; e.g., solid waste disposal problems resulting from FGD systems at electric power plants. Other cross-media impacts may be less obvious. Control systems that require additional steam or electricity to operate cause additional fuel to be burned resulting in increased emissions to the air, water, and land. Current environmental regulatory policy does not generally incorporate such cross-media impacts in a rigorous way. Rather, regulations

TABLE 1

POLLUTANTS REGULATED BY FEDERAL NEW SOURCE PERFORMANCE STANDARDS

Substance	Steam-Electric Generators	Petroleum Refineries	By-Product Coke Plants
AIR POLLUTANTS			
Carbon Monoxide		x	
Hydrocarbons		x	
Nitrogen Oxides	x		
Particulate Matter	x	x	P
Sulfur Dioxide	x	x	
Total Sulfur		P	
Hydrogen Sulfide		P	
WATER POLLUTANTS			
Ammonia		x	x
Biochem, Oxygen demand		x	x
Chemical Oxygen demand		x	
Chlorine Residual	x		
Chromium	x	x	
Corrosion Inhibitors	x		
Cyanides			x
Heat	x		
Oil and Grease	x	x	x
pH	x	x	x
Phenols		x	x
Sulfide		x	x
Total Organic Carbon		x	x
Total Suspended Solids	x	x	x
Zinc	x	x	
Copper	x		
Iron	x		
Phosphorus	x		

P = Proposed

typically focus on only a single pollutant emitted to a single medium.

An example of this is the NSPS for sulfur dioxide emissions from new steam generators. The current standard of 1.2 pounds per million Btu heat input to the boiler precludes direct combustion of coal without some type of pretreatment or post-treatment process in most cases. Currently available options are coal beneficiation (mechanical cleaning) and flue gas desulfurization (FGD). Alternative technologies are coal conversion processes producing clean gaseous or liquid fuels, such as low-Btu gas which can be burned directly as a boiler fuel or used in a combined cycle electric generating station. No NSPS yet exists limiting SO_2 emissions from combustion of gaseous fuels derived from coal. However, Table 2 shows that existing local, State, and Federal standards for other types of low-Btu gas containing hydrogen sulfide restrict emissions to levels an order of magnitude less than the NSPS for coal. This reflects the availability of technology to desulfurize low-Btu gas more extensively than is possible in combustion gases. A policy requiring best available control technology when burning low-Btu gas would substantially reduce SO_2 emissions relative to a conventional coal-fired system. However, one price of doing so might be a more energy intensive (as well as more expensive) technology, with greater multimedia impacts. This is illustrated quantitatively later in the paper.

TABLE 2

SELECTED SO_2 EMISSION STANDARDS FOR COMBUSTION OF FOSSIL FUELS

Source Category	Maximum Allowable Emission ($lbs\ SO_2/10^6\ Btu$)*		
	Solid	Liquid	Gas
Federal Standards (NSPS)			
Fossil-fueled steam Generators	1.2	0.8	--
Petroleum refinery plant gas	--	--	0.11^A
State and Local Standards			
Coke oven gas (Allegheny County, PA)	–	--	0.19^B
Fossil-fueled Steam generators			
(New Mexico)	0.34		0.16^C
(Wyoming)	0.2		--

^{A}From H_2S combustion assuming 250 Btu/scf (9.3 mJ/m^3)

^{B}From H_2S combustion assuming 700 Btu/scf (26.1 mJ/m^3)

^{C}For power plant associated with coal gasification plant

*1.0 lb/10^6 Btu = 0.430 kg/gJ

TABLE 3

COMPARISON OF FEDERAL WASTEWATER EFFLUENT STANDARDS

Petroleum Refineries	By-Product Coke Plants
Limits on 1-day and 30-day max.	Limits on 1-day and 30-day max.
Based on emission per unit of plant feedstock input	Based on emission per unit of plant feedstock output
Limits vary with plant size and complexity	Same limits for all plant sizes and complexity
Limits applicable to "end-of-pipe" (includes total plant)	Limits applicable only to coking process (not total integrated steel mill)

Finally, current new source standards do not necessarily regulate the same pollutant in the same way in different processes. An example is the difference in the way wastewater effluent limitations are imposed on petroleum refineries and by-product coke manufacturing plants, two currently regulated processes that bear similarities to coal conversion plants. Table 3 shows that in most respects the structure of current regulations for these two processes differ substantially even though most of the regulated pollutants are identical, and the level of allowable emissions are similar when normalized on the input fossil fuel energy content. The structure of future regulations for coal gasification and liquefaction plants is more uncertain since the zero discharge goal of the 1972 Federal Water Pollution Control Act may require complete recycling of all wastewaters from these facilities. Again, cross-media environmental impacts (on land and air) will result from wastewater control strategies. These must be anticipated in the design of wastewater regulations.

METHODOLOGICAL NEEDS FOR REGULATION DEVELOPMENT

The discussion above suggests a number of policy research questions that the authors have raised previously in the context of regulatory policy implications for synthetic fuel plants.(1) These include questions as to how plant type, size, complexity, and product mix should enter the regulatory picture; whether limits on pollutant discharge should be established for individual unit operations or for larger systems, including the total plant; whether environmental regulations can be structured so as to reward process improvements that reduce environmental impact; and whether a multi-media approach that minimizes overall environmental impact can be developed into a workable regulatory scheme.

Evaluation of environmental tradeoffs, however, is a difficult task. An idealized framework for such an analysis is suggested in Figure 1. The three principal elements involve: (a) characterizing the rates and types of emissions to air, water, and land as a function of the coal feed type and the characteristics of process and environmental control technologies; (b) examining how these emissions are transferred through various media (air, land, and water) to receptors in the environment (humans, plants, and animal life); and (c) evaluating the damage incurred by these receptors from exposure to the various pollutants. This type of methodology would yield a benefit/risk/cost analysis of alternative regulatory standards, in contrast to the existing philosophy of NSPS which is based only on best available technology. The framework is idealized, however, since our current state of knowledge is simply inadequate to actually perform this type of analysis. Indeed, even the characterization of coal conversion process emissions cannot yet be done rigorously in many cases.

Three research programs in progress at Carnegie-Mellon University (CMU) seek to improve methodologies for assessing coal conversion plant environmental impacts and regulatory policies. One effort involves the measurement and characterization of waste streams from ERDA pilot plants producing high-Btu gas from coal.(3) This program will contribute a substantially improved data base for assessing advanced technologies and the implications of alternative policy formulations. A

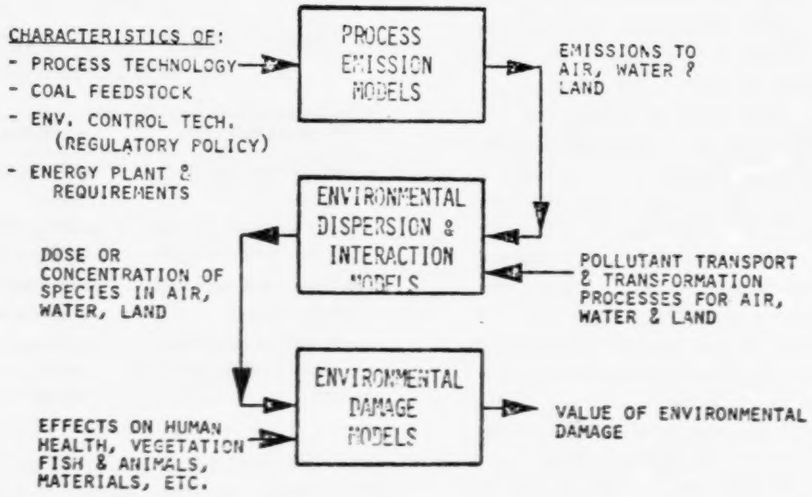

CHARACTERISTICS OF:
- PROCESS TECHNOLOGY
- COAL FEEDSTOCK
- ENV. CONTROL TECH. (REGULATORY POLICY)
- ENERGY PLANT & REQUIREMENTS
PROCESS EMISSION MODELS
EMISSIONS TO AIR, WATER & LAND
ENVIRONMENTAL DISPERSION & INTERACTION MODELS
DOSE OR CONCENTRATION OF SPECIES IN AIR, WATER, LAND
POLLUTANT TRANSPORT & TRANSFORMATION PROCESSES FOR AIR, WATER & LAND
ENVIRONMENTAL DAMAGE MODELS
EFFECTS ON HUMAN HEALTH, VEGETATION FISH & ANIMALS, MATERIALS, ETC.
VALUE OF ENVIRONMENTAL DAMAGE

Figure 1. An idealized framework for standards development.

second program is directed at assessing the environmental damage of pollution with particular emphasis on the role of uncertainty. To date, this research has focused on the health effects of sulfur dioxide emissions from coal-fired power plants.[4] A third effort, which is the subject of the present paper, involves the development of a systematic framework for characterizing air, water, and land emissions from coal utilization technologies as a function of four factors:

- coal characteristics,
- process and environmental control technology characteristics,
- environmental regulatory constraints, and
- useful product or output.

This represents the first module in Figure 1. The emission inventories derived from this analysis are basic to any subsequent approach to integrate their impact on air, land, and water. Currently, work is focused on conventional and advanced coal-to-electric systems, which represent the greatest potential for coal use in the near term.

COAL-TO-ELECTRIC SYSTEMS MODEL

A systematic framework for comparing alternative coal-to-electric technologies is illustrated in Figure 2. The figure applies to a mine mouth situation using run-of-mine (ROM) coal in one of several ways. One is to burn the coal directly in a conventional steam-electric generator using once-through cooling and no flue gas cleanup. This would represent an environmentally uncontrolled or "base case" situation. A system designed to meet environmental standards would be more complex. To meet water effluent standards for heat, suspended solids, organics, and other chemical species a wastewater treatment system including cooling towers or pond would replace simple once-through cooling. To meet air pollution standards, a flue gas treatment system or coal cleaning prior to combustion would be required. Flue gas treatment could include a desulfurization system (FGD) and/or a particulate removal device (mechanical collector, electrostatic precipitator or baghouse). Precombustion cleanup could include

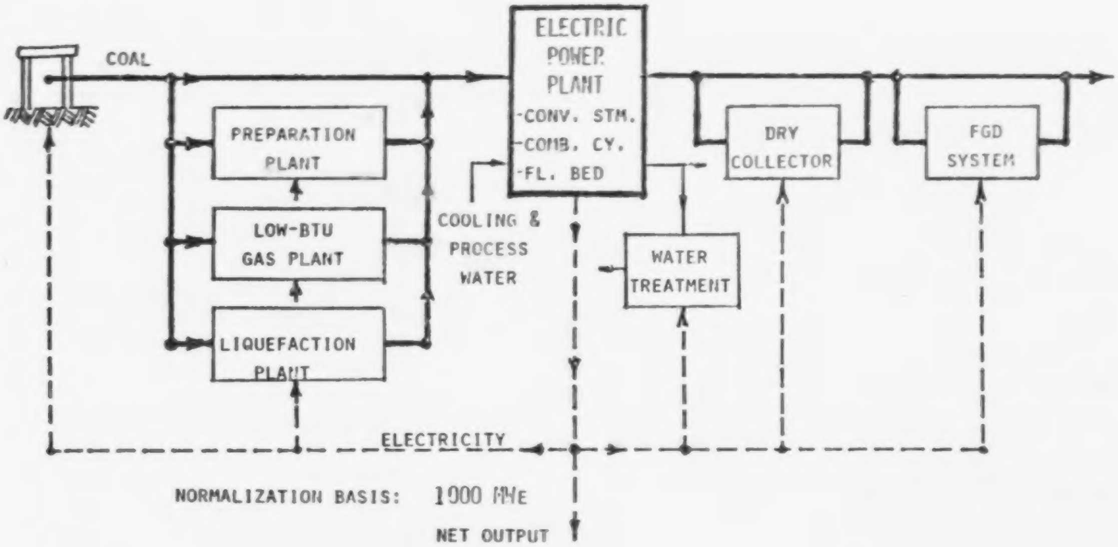


Figure 2. CMU systems model of coal-to-electric technologies.

mechanical coal cleaning or conversion of coal to a clean gaseous or liquid fuel. Advanced technologies such as fluidized bed boilers offer the potential for direct combustion of coal with simultaneous pollutant removal.

All the alternatives above have two important characteristics. First, in meeting environmental regulations for air and water pollutants additional residual streams appear that may pose new environmental problems. Secondly, each component or system alters the thermal efficiency of the coal-to-electric cycle, directly affecting all material flow rates (including effluents to air, land, and water) associated with the production of power. From an environmental point of view, the systems model in Figure 2 asserts that the proper basis for comparing different coal-to-electric generating systems is on the ability to produce the same amount of electricity for sale after all ancillary energy needs are accounted for. For convenience this quantity is taken as 1000 MW. Electricity is thus viewed as a socially desirable commodity and the environmental impacts of different systems producing it are compared on the basis of *a common net output*. From this perspective, a number of technical and policy issues can be addressed as indicated in Table 4. The goal of on-going research at CMU is to develop computerized

TABLE 4

EXAMPLES OF ENVIRONMENTAL IMPACT TRADEOFF ISSUES ADDRESSED BY PARAMETRIC ANALYSIS USING CMU MODEL

Useful Electrical Output	Coal Characteristics	Emissions Contraints	Process and Env. Control Tech. Characteristics	Types of Questions Addressed
Constant	Varied	Constant	Derived	What process and/or control technology characteristics are needed to comply with fixed emission constraints for various coals? What are the associated coal production rates, costs, and emissions of pollutants to air, land and water from producing a fixed amount of electricity for sale?
Constant	Derived	Constant	Varied	What coals can be used to comply with given emission regulations for different processes or facility configurations? What are the associated costs and emissions?
Constant	Derived	Varied	Constant	What coals can be used at a given type of facility as emission constraints are changed? What are the associated costs and emissions?
Constant	Varied	Derived	Constant	What regulations are required in order to use certain types of coal at a given facility? What are the associated costs and emissions?
Constant	Constant	Varied	Derived	What facility characteristics are required to process a given coal for various emission constraints? What are the associated costs and emissions?
Constant	Constant	Derived	Varied	What must the emission constraints be for various facilities in order to process a given coal? What are the associated costs and emissions?

analytical models of the modules in Figure 2 which are sufficiently detailed to capture all pertinent factors, but which are also sufficiently simple and flexible so that a wide range of parameters can be examined easily. The following paragraphs present highlights of the models currently developed. Following this is an illustration of their use to examine the multimedia impacts of alternative formulations of SO_2 regulations for coal-based electric power systems.

Coal Feedstock Parameters

Four coal characteristics are the principal parameters of the model. These are the coal higher heating value, ash content, sulfur content, and pyrite fraction expressed on a dry mass basis. More detailed data on coal composition (ultimate analysis) is used to model the performance of FGD and low-Btu gasification systems. The electrical energy penalty required to mine coal (applicable to underground mining) is also an optional parameter of the model.

Coal Preparation Plant

Mechanical cleaning of coal prior to combustion is modeled in terms of either a "simple" plant, designed principally for ash reduction with maximum energy yield and some sulfur reduction, or a "complex" plant providing greater sulfur reduction but with higher material and energy losses. Figure 3 shows the latter configuration. Wash circuits are provided for coarse and fine coal, with the fine stream reporting to a thermal dryer to achieve an acceptable moisture content in the final coal mixture. In the analytical model, ash, sulfur, and energy recovery are functions of the overall material yield (which depends on bath specific gravity) and the crushed coal top size. The model employs coal-specific washability curves of the type reported by the U.S. Bureau of Mines for various domestic coal seams.(5) Electrical energy is required by the plant for coal crushing, particulate control equipment, materials handling, liquid pumping, and wastewater treatment. These requirements are evaluated and modeled in proportion to the coal flow in various circuits. The thermal dryer incurs an additional energy penalty modeled as a fraction of the ROM coal input. Air pollutant emissions from the dryer incorporate empirical data on adsorption of SO_2 on the dried coal and levels of NO_x emissions. Dryer TSP emissions are controlled to the NSPS level assuming use of a wet scrubber. Solid waste from the cleaning plant occurs as a dewatered sludge principally containing ash, sulfur, and coal refuse. All other waters are assumed to be completely recycled.

Figure 4 illustrates the sulfur reduction achieved for three eastern coals "processed" through the CMU coal cleaning plant model. In this case the plant was designed to recover 90 percent of the input coal mass with coal crushed to 3/8" top size. 63-68 percent of the sulfur was pyritic. The plant achieved an overall reduction of 38 to 41 percent in total sulfur expressed as equivalent SO_2 per unit energy content of coal. Between 3 and 8 percent of the coal energy was lost as plant refuse.

Steam-Electric Generator

The nominal steam-electric system assumed in the CMU model employs a pulverized coal boiler designed to achieve NSPS levels of NO_x emissions. The primary electrical conversion efficiency is represented as a gross cycle heat rate, defined as the electrical generator output excluding any energy needed to run coal production and environmental control systems. The primary coal pulverizer is treated separately since its energy requirement decreases when coal is mechanically cleaned prior to combustion. A penalty for nitrogen oxide control can be included if boiler modifications such as air preheater bypass are needed to achieve emission standards.

Coal ash and sulfur streams are partitioned between the bottom ash and flue gas streams while thermal heat loss is divided between air and water. This determines the emissions of an uncontrolled plant. Emissions of carbon monoxide, hydrocarbons and nitrogen oxides are calculated from empirical emission factors for the assumed boiler type. Solid waste streams from an uncontrolled plant are assumed to occur as boiler bottom ash and sludge from the feedwater treatment unit. These are calculated by mass balance and empirical effluent factors, respectively. Uncontrolled effluents to receiving waters include thermal and

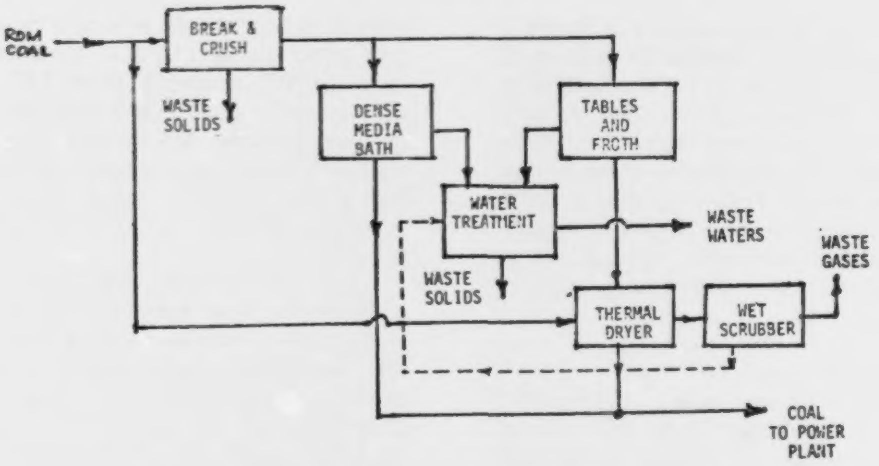

ROM COAL
BREAK & CRUSH
WASTE SOLIDS
DENSE MEDIA BATH
TABLES AND FROTH
WATER TREATMENT
WASTE WATERS
WASTE GASES
WASTE SOLIDS
THERMAL DRYER
WET SCRUBBER
COAL TO POWER PLANT

Figure 3. Schematic of coal cleaning plant model.

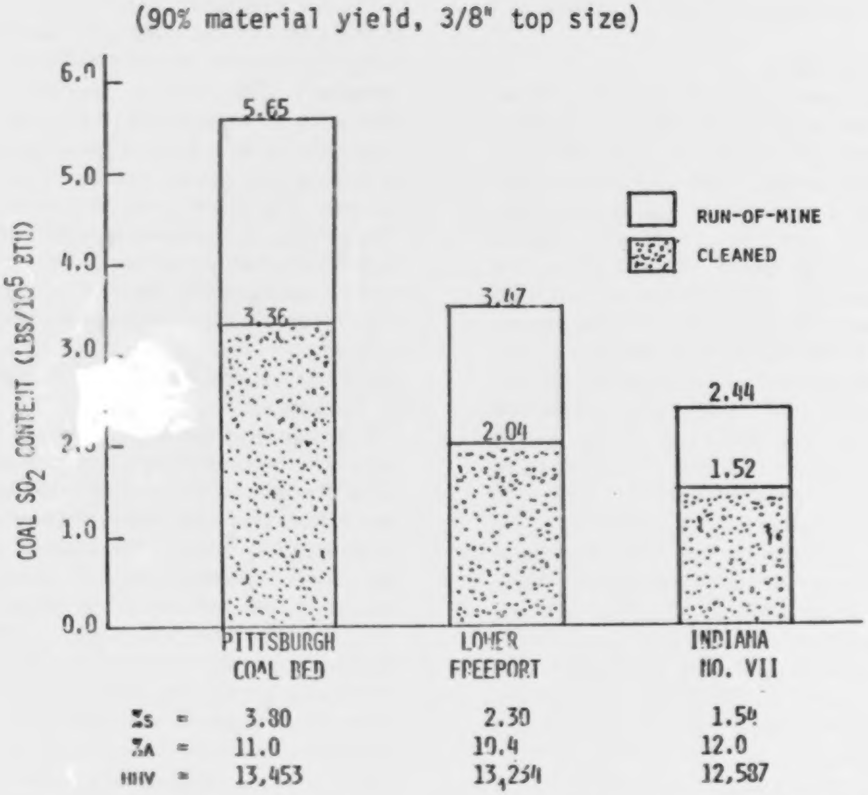


Figure 4. Sulfur content of three eastern coals "cleaned" by model plant.

chemical discharges plus suspended solids. These are estimated from available data on power plant characteristics.

Particulate Collection System

Flyash is assumed to be collected in a dry collection system and/or a wet scrubber incorporated as part of an FGD system. The dry collector can be an inertial separator, baghouse, or electrostatic precipitator. Performance is represented in terms of a collection efficiency with an associated energy penalty expressed as a fraction of gross power plant output. The mass flow rate of solid waste is determined by a mass conservation algorithm that includes a specified moisture content for slurried systems.

Flue Gas Desulfurization System

The performance of an FGD system can be modeled simply by specifying an SO_2 removal efficiency and associated energy penalty. Alternatively, a detailed analytical model has been developed which calculates FGD energy requirements for a nonregenerative limestone system, which is the most prevalent FGD technology today. This model is similar to one developed by the Tennessee Valley Authority (TVA) for cost estimation in lime/limestone FGD systems,[6] and employs performance correlations developed by Bechtel and TVA. The schematic of Figure 5 shows the major elements of the model. Where dry particulate collection is used, partial bypass of the scrubber can be implemented to achieve current SO_2 emission standards by treating only a fraction of the gas to a higher SO_2 removal efficiency than needed if the entire flue gas stream is scrubbed. Sensitivity analyses have shown that this can result in significant energy as well as cost savings.[7] Energy penalty calculations incorporate raw material and sludge-handling costs as well as electrical requirements for all gas-phase and liquid-phase fans and pumps plus steam requirements for gas reheat.

Figure 6 illustrates the fact that FGD energy requirements increase nonlinearly as SO_2 emissions are decreased. The figure also indicates how higher sulfur coals incur greater energy penalties to achieve a given SO_2 emission standard. The absolute level of energy needed depends on a number of coal, plant, and system parameters as suggested in Table 5. The principal secondary enviromental impact of lime/limestone technology is sludge consisting principally of calcium sulfate, calcium sulfite, flyash, and limestone with appreciable moisture content. Regenerative systems that eliminate sludge disposal incur a significantly larger energy penalty. This increases the air

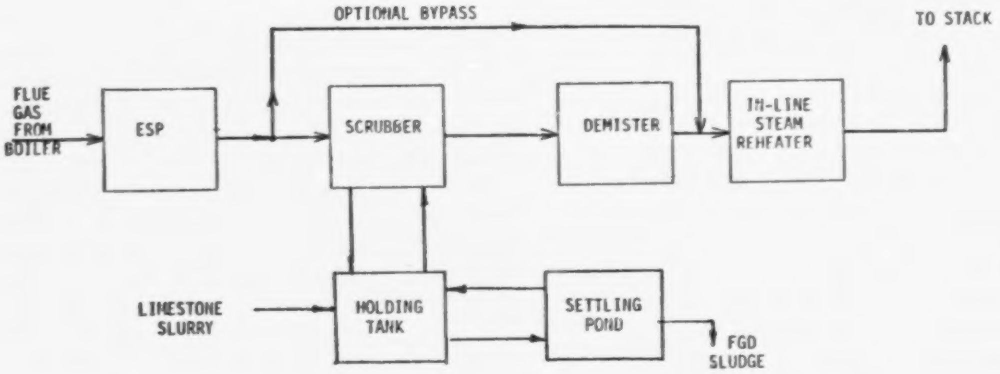


Figure 5. Schematic of limestone FGD system.

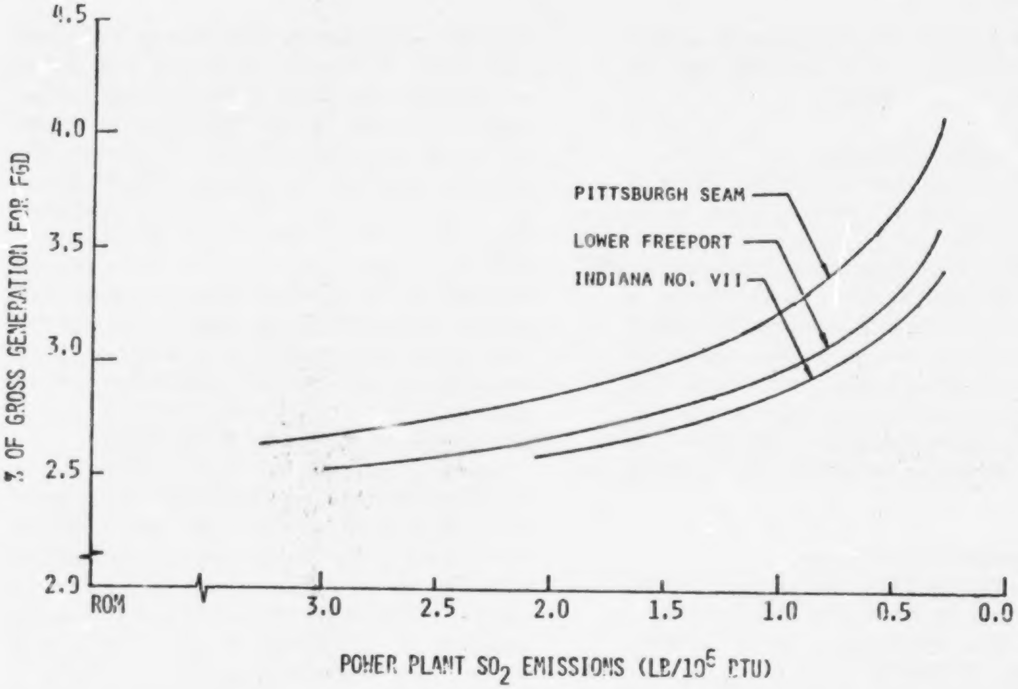


Figure 6. FGD system energy requirements for three eastern coals.

TABLE 5

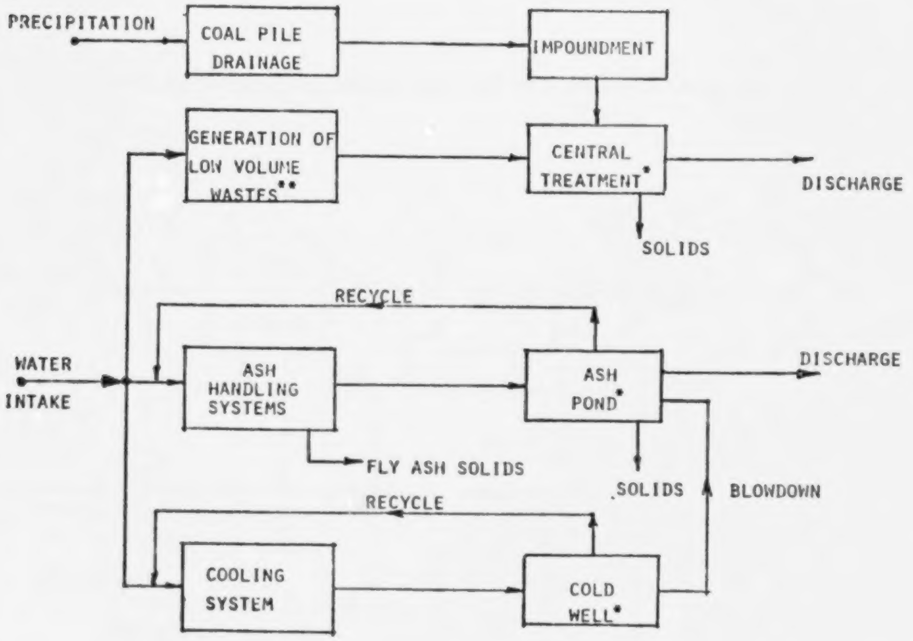
EFFECT OF SYSTEM PARAMETER VARIATIONS ON LIMESTONE FGD SYSTEM ENERGY REQUIREMENTS
(Ref. 6)

Parameter	One Percent Increase in Nominal Value	Resulting Percent Increase in FGD Energy*
Stack exit temperature	1.75°F	2.3
Coal heating value	105 Btu/lb	-1.6
Coal sulfur content	0.035%	0.7
SO_2 emission regulation	0.012 lb/10^6 Btu	0.52
Entrainment at demister	0.001% gas wt.	0.45
Scrubber inlet temperature	3.0°F	-0.4
Gross plant heat rate	90 Btu/KWH	-0.1

pollutant and ash emissions per unit of net electrical output.

Water Treatment System

Water treatment systems for conventional steam-electrical power plants are designed to achieve effluent standards for heat, suspended solids, and other chemical constituents (see Table 1). The principal component is a cooling tower which transfers waste heat from the water to the air. This system incurs an energy penalty modeled principally in terms of the water pumping head, cooling range, and increase in turbine back-pressure imposed by the tower. Schemes for the treatment of chemical wastes are modeled in different forms depending on whether the cooling water treatment


PRECIPITATION
COAL PILE DRAINAGE
IMPOUNDMENT
GENERATION OF LOW VOLUME WASTES**
CENTRAL TREATMENT*
DISCHARGE
SOLIDS
RECYCLE
WATER INTAKE
ASH HANDLING SYSTEMS
ASH POND*
DISCHARGE
FLY ASH SOLIDS
SOLIDS
BLOWDOWN
RECYCLE
COOLING SYSTEM
COLD WELL*

*COAGULANTS MAY BE ADDED

**INCLUDES BOILER BLOWDOWN, EQUIPMENT CLEANING WASTES (BOILER TUBES, BOILER FIRESIDE, AIR PREHEATER, STACK, COOLING TOWER BASIN), RAINFALL RUNOFF, SANITARY WASTES, PLANT LAB AND SAMPLING STREAMS, INTAKE SCREEN BACKWASH, AND FLOOR DRAINS.

Figure 7. Water treatment for a controlled plant using a recirculating system.

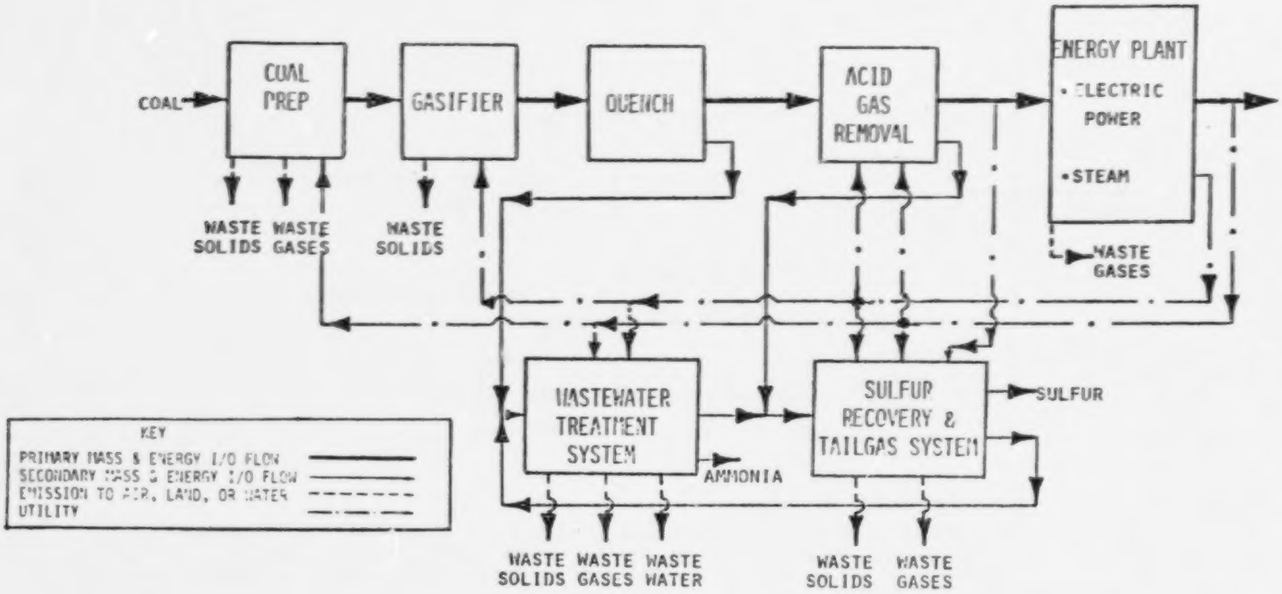
system is of the recirculating or once-through type. One example is shown in Figure 7. Note that treatment of chemical waste transforms potential wastewater effluents into sludges to be disposed on land.

Coal Gasification/Combined Cycle System

A potential alternative for using coal to produce electricity is to first gasify it, then use the low-Btu gas either as a boiler fuel in a conventional Rankine cycle or in a combined cycle system having the advantage of a higher thermodynamic efficiency. Although commercial low-Btu gasifiers are available the combined cycle approach has yet to be successfully demonstrated. Nonetheless, electricity from coal via low-Btu gas could become an attractive alternative to direct combustion if theoretical efficiency advantages can be realized economically.

A generic model of a low-Btu gasification plant (Figure 8) has been developed from published studies of various processes.(8-12) Run-of-mine coal first enters a preparation stage where it is crushed and sized. Pretreatment (mild oxidation) may also occur at this point when using agglomerating coals. Coal is then introduced into the gasifier with additional water (steam) and air to generate crude product gas. This gas is cooled in a quench stage to remove heavy liquids, particles, and other im-

Figure 8. Energy and mass flows for low-Btu coal gasification/combined cycle model.


COAL
COAL PREP
GASIFIER
QUENCH
ACID GAS REMOVAL
ENERGY PLANT
• ELECTRIC POWER
• STEAM
WASTE SOLIDS
WASTE GASES
WASTE SOLIDS
WASTE GASES
WASTEWATER TREATMENT SYSTEM
AMMONIA
SULFUR RECOVERY & TAILGAS SYSTEM
SULFUR
WASTE SOLIDS
WASTE GASES
WASTE WATER
WASTE SOLIDS
WASTE GASES
KEY
PRIMARY MASS & ENERGY I/O FLOW
SECONDARY MASS & ENERGY I/O FLOW
EMISSION TO AIR, LAND, OR WATER
UTILITY

SOME POTENTIAL POLLUTANTS FROM
SYNTHETIC FUELS PLANT

AIR	WATER	LAND
SO_2	NH_3	ASH SLURRIES
TSP	ΦOH	FINES
NO_x	CN	DRY RESIDUES
CO	SCN	WASTE TREATMENT SLUDGES
C_xH_y	BOD	
H_2S	COD	SPENT CATALYST
COS	TOD	SLAGS
NH_3	TSS	
HCL	TDS	
HCN	pH	
TRACE METALS	HEAT	
CARCINOGENS	OILS	

purities. The cleaned gas then proceeds to the acid gas removal step where the sulfur concentration is reduced to an acceptable level dictated by environmental regulatory policy. The gas can then be fired in a boiler or utilized in a combined cycle system to produce electric power. Waste gases are exhausted to the atmosphere just in a conventional plant. The two major environmental control systems introduced by the low-Btu gasification process are the wastewater treatment system and the sulfur removal/recovery system.

Wastewater Treatment. The characteristics of raw wastewaters from advanced coal gasification plants are not yet well characterized although some pilot plant data are becoming available.(13,14) Table 6 suggests that while there is some simlarity among gasification process effluents there are also marked differences from one process to another that can significantly affect the level of type of wastewater treatment technologies. In general, treatment will include oil-water separation; steam stripping to remove hydrogen sulfide (which is sent to the sulfur recovery system); ammonia (recovered as a by-product) and other acid-producing dissolved gases; and removal of organic compounds, particularly phenols, using an absorption system (for wastewaters with low organic content) and/or a biological oxidation system (for wastewaters with high organics). A polishing process may also follow. It remains unclear, however, as to what level of treatment will apply to commercial gasification plants. Presently, these are subject only to State and local standards, which vary considerably. Rubin and McMichael(11) showed that Federal NSPS standards for by-product coking and petroleum refinery—two processes resembling coal gasification plants—are similar when compared on the basis of fossil fuel energy input to the process (Table 7). It remains speculative as to whether this might also apply to coal gasification processes. Several processes under development call for the complete recycle of wastewaters to improve the process design as well as to comply with potential zero discharge requirements for liquid waste.

In terms of the cross-media problem, the important point to emphasize is that control or elimination of wastewater constituents aggravates air and land problems indirectly via the need to produce additional electricity and steam, as well as directly through the production of gaseous and solid waste discharges (sludges) from various unit operations. Electrical energy penalties are incurred in pumping wastewaters through the various treatment steps, while steam is needed for stripping

TABLE 6

WASTEWATER CHARACTERISTICS OF THREE
COAL CONVERSION PROCESSES
(Ref. 14)

POLLUTANT	Synthane Process PDU, (North Dakota Lignite)	Hygas Process Pilot Plant (Montana Lignite)	By-Product Coke Comm'l Plant (Bituminous)
Ammonia	19.5 ± 3.0	13.1 ± 0.3	8.5
Phenol	11.9 ± 1.2	11.4 ± 2.4	0.9 - 1.0
Chemical Oxygen Demand	77.7 ± 14.4	N/D	4.0 - 5.5
Total Organic Carbon	22.0 ± 3.0	39.1 ± 15.4	1.6 - 2.0
Cyanide	Negligible	Negligible	0.02 - 0.05
Thiocyanate	0.05 ± 0.08	2.5 ± 0.2	0.3 - 0.4
Tar	74.1 ± 27	~0	93
Light Oil	N/A	N/A	33
Total Dissolved Solids	N/A	12.4 ± 0.06	N/A

TABLE 7

ADJUSTED NEW SOURCE PERFORMANCE STANDARDS FOR BY-PRODUCT COKE MAKING AND PETROLEUM REFINING

(30-Day Maximum) (Ref. 1)

(pounds of pollutant per 10^{12} Btu feedstock)

Pollutant	Petroleum Refineries	By-Product Coke Making
BOD 5	210-2900	N/A
TSS	140-1920	600
COD	1050-20,000	N/A
Oil & Grease	70-890	240
Phenolics	1.5-19	12
Ammonia as N	40-1700	240
Sulfide	1.1-16	5.8
Total Chromium	3.5-47	N/A
Hexavalent Chromium	0.06-0.80	N/A
Cyanides amenable to Chlorination	N/A	5.8

- Assumes heating values of 6.5 million Btu/bbl for crude oil and 12,000 Btu/lb for coal, with a coke yield of 0.69 lb coke/lb coal.

N/A = not applicable.

operations. This steam may or may not represent an energy penalty, depending on details of process design. This is illustrated quantitatively later in this paper. In all cases, the magnitude of the ancillary energy demand is proportional to the quantity of wastewater treated.

Sulfur Removal and Recovery. Whereas high-Btu gasification processes must remove virtually all gaseous sulfur to prevent poisoning of catalysts and maintain gas quality, removal of sulfur from low-Btu gas producing steam or electricity is needed only to comply with environmental standards. As many as three unit operations may be involved in controlling sulfur emissions: acid gas removal, primary sulfur recovery, and tail gas cleanup system. Figure 9 shows how the energy penalty for increased desulfurization increases nonlinearly for one acid gas removal system in widespread use.(15) Table 8 shows the overall energy requirement incurred in product gas desulfurization using several systems analyzed for the EPA. Environmental impacts of desulfurization may occur as gaseous emissions notably sulfur compounds from the tailgas treatment system and solid waste generation in the form of sludges

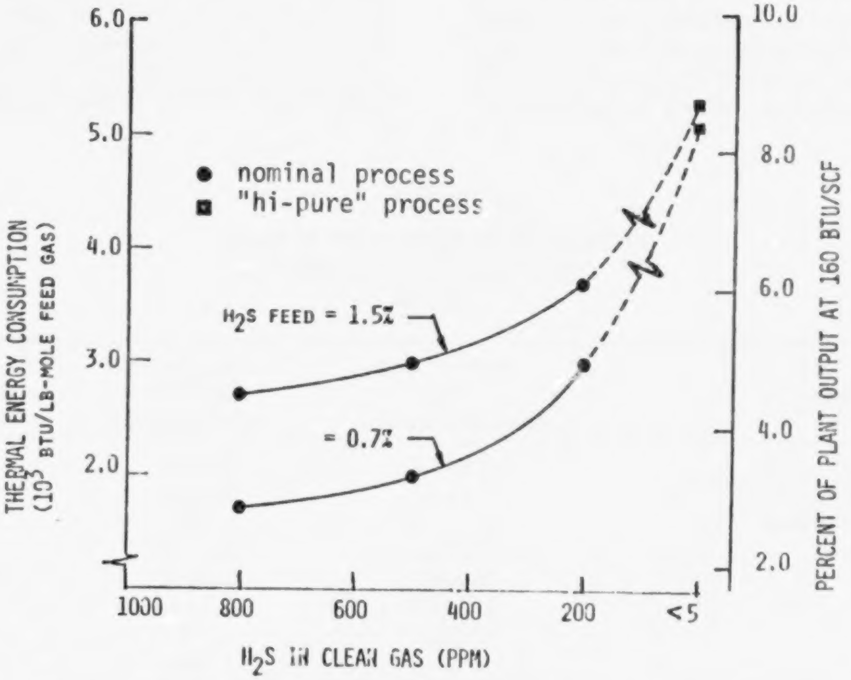


Figure 9. Thermal energy requirement for acid gas removal (Benfield Process) (Ref. 20).

TABLE 8

LOW-BTU GASIFICATION PLANT

4.5% Sulfur Feedstock, 137 x 10^3 GJ/day

ENERGY REQUIREMENTS FOR SULFUR REMOVAL/RECOVERY*

(As a percent of product gas output)

Process Component	Hot Potassium +Claus Plant +Beavon Tailgas	Hot Potassium + Claus Plant +Wellman-Lord TG	Iron Oxide +Allied Plant +Beavon Tailgas
Sulfur Content =	0.7 KG/GJ (0.3 lb $SO_2/10^6$ Btu)	0.7 KG/GJ (0.3 lb $SO_2/10^6$ Btu)	3.0 KG/GJ (1.2 lbs $SO_2/10^6$ Btu)
SULFUR RECOVERY			
Electricity	1.91	1.91	9.60
Steam	9.34	9.34	–
Sub-Total	11.25	11.25	9.60
TAILGAS CLEANUP			
Electricity	0.28	0.48	0.12
Steam	0.04	0.17	0.02
Auxillary Fuel	0.61	5.11	0.09
Sub-Total	0.93	5.76	0.22
Total Gas Energy	12.2%	17.0%	9.8%
GJ/10^3 KG S Removed	64.7	92.0	59.0
Plant Cost-¢/GJ	20.2	24.3	32.4
(¢10^6 Btu)	21.3	25.6	34.2

*Derived from Ref. 9 assuming efficiencies of 40% for electricity, 85% for steam and 100% for auxiliary fuel.

and spent catalyst. Additional liquid waste may be generated and sent to the wastewater control section.

APPLICATION OF ANALYTICAL MODELS

Impact of SO_2 Emission Regulations

The models described above can be used to systematically compare the multimedia impacts of different technologies generating electricity, as well as the cross-media effects of alternative regulatory strategies. To illustrate this, consider the regulation of sulfur dioxide emissions from a conventional power plant burning a high sulfur eastern coal (Pittsburgh seam, Figure 4). Define a "base case" plant configuration as one with no desulfurization technology and no cooling tower or water treatment system producing 1000 MW net output. Compare this to an equivalent environmentally controlled plant that meets Federal new source standards for water pollutants, and controls SO_2 emissions to some specified value expressed as mass emission per unit heat input to the boiler. Figure 10 shows that water pollutants are now virtually eliminated while the SO_2 mass emission is reduced up to 90 percent depending on the emission level that is specified.

Cross-media consequences of these emission reductions are shown in Figures 11-15, assuming use of cooling towers and limestone FGD.

Figure 11 shows an increase in the net cycle heat rate of the power plant corresponding to a decrease in overall thermal efficiency from about 38 percent for the base case plant to about 33 percent for a controlled plant meeting NSPS levels for water and SO_2 emissions (Figure 12). If the coal is mechanically cleaned before combustion the FGD energy penalty is reduced but the overall cycle heat rate (mine-to-busbar) is still higher because approximately

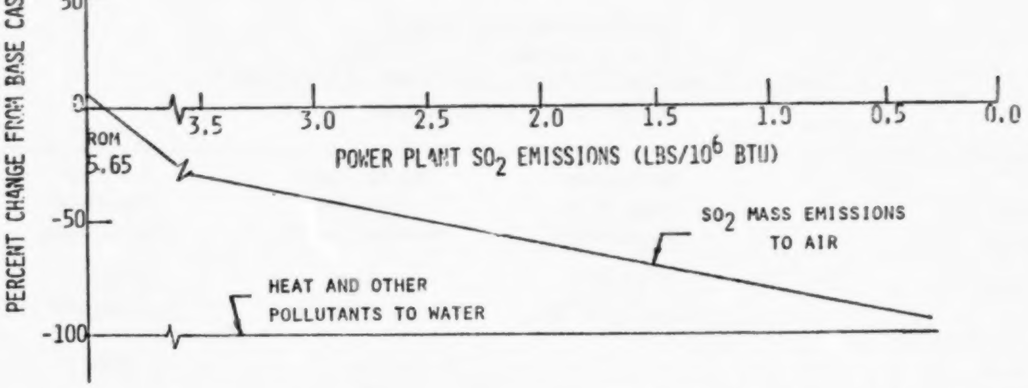


Figure 10. Effect of emission standards on base case SO_2 and water pollutant emissions. (Pittsburgh seam coal)

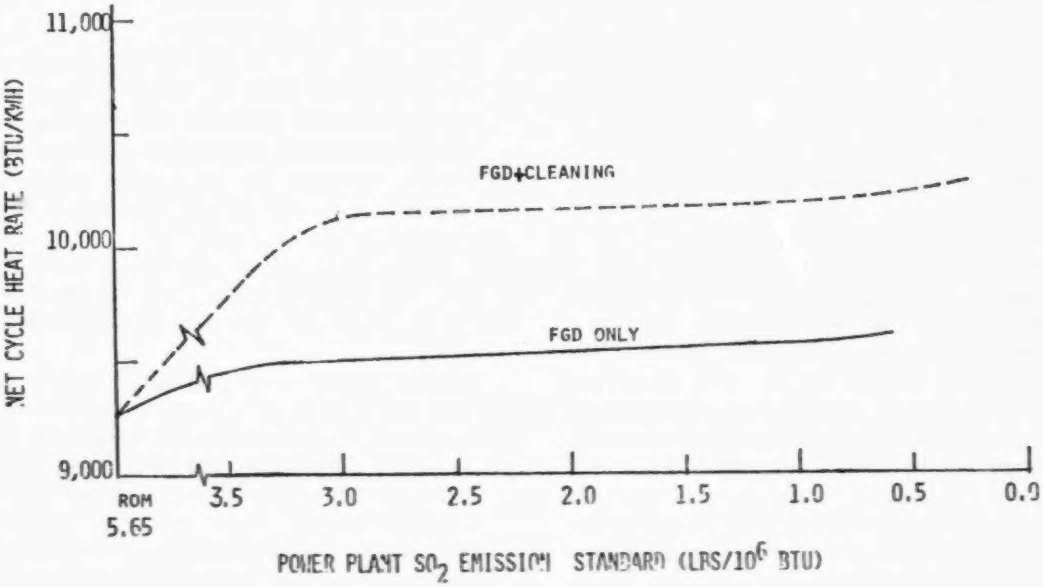


Figure 11. Effect of SO_2 emission standard on net cycle heat rate. (Pittsburgh coal)

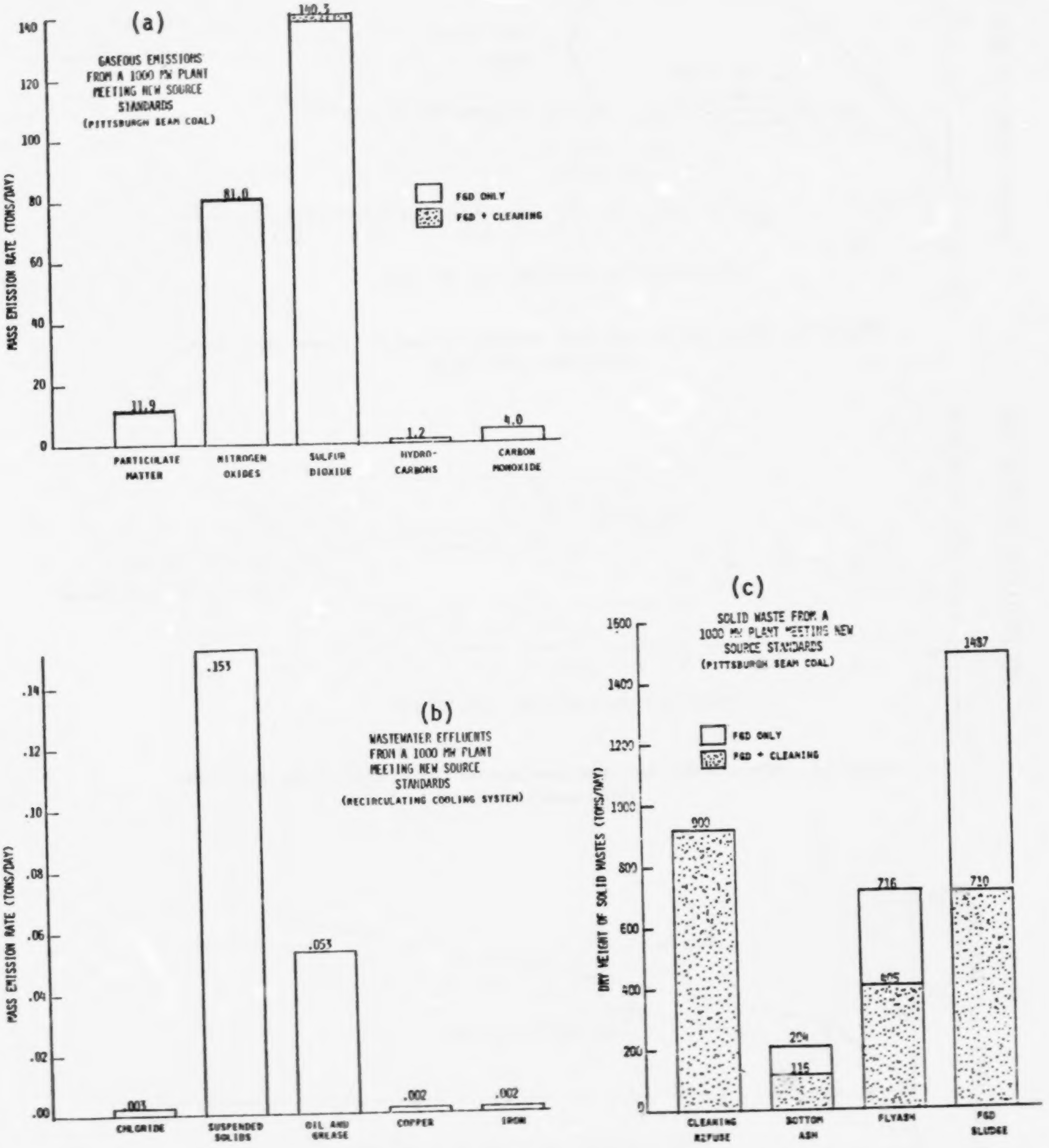


Figure 12. Multimedia pollutant emissions for a plant meeting NSPS levels at 1000 MW net output with Pittsburgh seam coal.

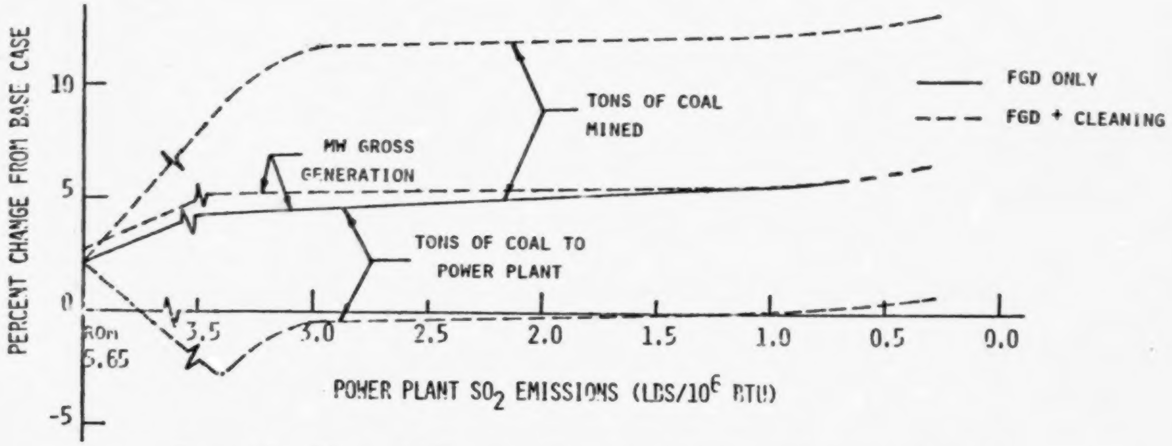


Figure 13. **Effect of SO$_2$ emission standard on coal and power production. (Pittsburgh seam coal)**

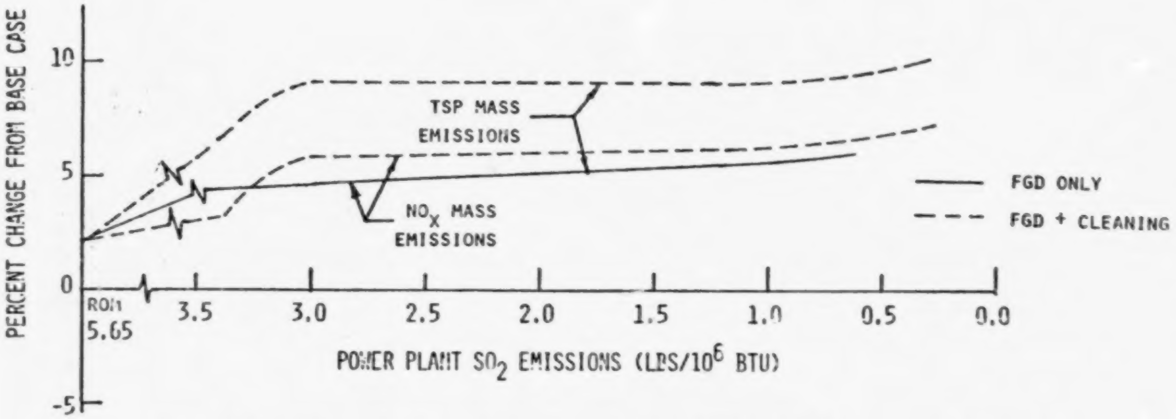


Figure 14. **Effect of SO$_2$ emission standard on TSP and NO$_x$ mass emissions. (Pittsburgh seam coal)**

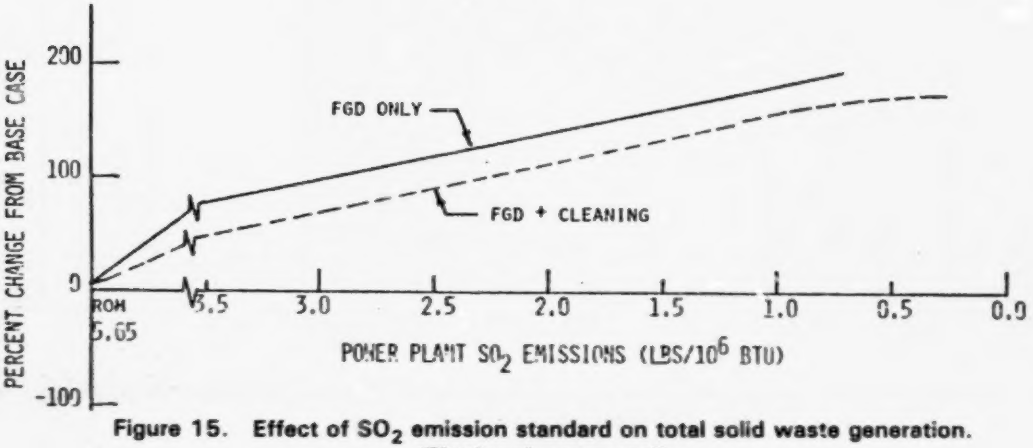


Figure 15. **Effect of SO$_2$ emission standard on total solid waste generation. (Pittsburgh seam coal)**

5 percent of the coal energy is lost during the cleaning process. Figure 1 shows how this is reflected in increased coal tonnage that must be mined to maintain the same net power output. Although more coal must be mined using cleaning, the mass of coal delivered to the power plant decreases since washing concentrates the recovered energy in less mass. As the SO_2 regulation becomes more stringent more coal must be fired to maintain the same net power plant output because of the increasing ancillary energy needed for FGD and cleaning plant equipment.

As a result of increased coal demand, particulate (TSP) and nitrogen oxide (NO_x) mass emissions also increase nonlinearly as the SO_2 regulation is tightened (Figure 14). Both TSP and NO_x are assumed to meet the current NSPS levels in all cases. Since these are given in terms of boiler energy input, the absolute mass emission still increases as more coal is fired to the boiler. Figure 15 shows that solid waste generation increases most dramatically as SO_2 emission levels are lowered. In this Figure, solid waste is taken to include the sum of all cleaning plant refuse plus all power plant wastes (principally FGD sludge, flyash, and bottom ash). On a dry basis, the quantity of solid waste increases approximately 180 percent as sulfur emissions are reduced from their uncontrolled value to the NSPS value using this particular coal. This does not include the substantial loss of water that also occurs since cleaning plant and FGD sludge typically contain only 40-50 percent solids by weight.

Interpretation of BACT

Another aspect of SO_2 regulatory policy having cross-media implications concerns the recent Congressional requirement that best available control technology (BACT) be used to reduce power plant sulfur emissions. Two common interpretations of BACT include a fixed emission standard less than the present NSPS (e.g., 0.6 pounds of SO_2 per million Btu), or a constant percent reduction in sulfur (e.g., an 80 percent FGD efficiency, reflecting 90 percent SO_2 removal with 90 percent reliability).(2) Figures 16 and 17 show the impact on dry solid waste and sulfur dioxide mass emissions when these two interpretations of BACT are applied using three eastern coals (from Figure 4), and assuming limestone FGD with and without coal cleaning. Mass emissions are displayed as a function of the fired coal sulfur content expressed as equivalent sulfur dioxide per unit energy input.

One sees that as the input sulfur content decreases, a standard calling for constant removal efficiency results in less SO_2 emissions to the atmosphere as opposed to the fixed emission standard. For the coals modeled here, the lowest sulfur levels are obtained only by cleaning coal prior to combustion. For coals of higher sulfur content the constant FGD removal efficiency yields greater SO_2 emissions than the fixed emission level. This suggests that if an overriding objective of national environmental policy is to minimize sulfur dioxide emissions, regulations should require the more stringent of a constant removal efficiency and fixed emission standard. In such a case, the practical limitations of FGD technology may require higher sulfur coal to be washed prior to combustion. High sulfur coals with no appreciable pyrite content (hence, not subject to washing) could become unusable.

The cross-media impacts associated with BACT were illustrated earlier for one particular coal. Figure 1 shows one effect (on total solid waste generation) for three eastern coals, with and without coal washing. Note that while the combined solid waste of the cleaning and power plants decreases when the high sulfur (Pittsburgh seam) coal is washed before combustion, the reverse is true for the lowest sulfur (Indiana No. VII) coal. Total waste using the median sulfur coal also increases slightly when both FGD and cleaning are used. In all cases more *total* solid waste is generated when washing is used to achieve a given *inlet* SO_2 content. Details of solid waste impacts will vary with the types and washability characteristics of local coals and their geographical relationships to mine and power plant.

Comparison of Conventional and Gasification Combined Cycle Systems

Though the lack of data for operating gasification/combined cycle systems precludes

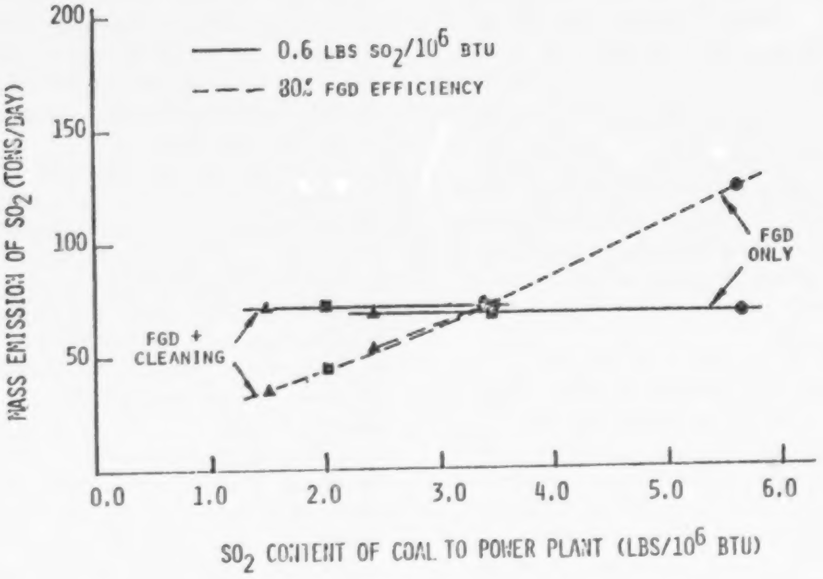


Figure 16. Effect of SO_2 regulation on SO_2 mass emissions for three eastern coals (1000 MW ne

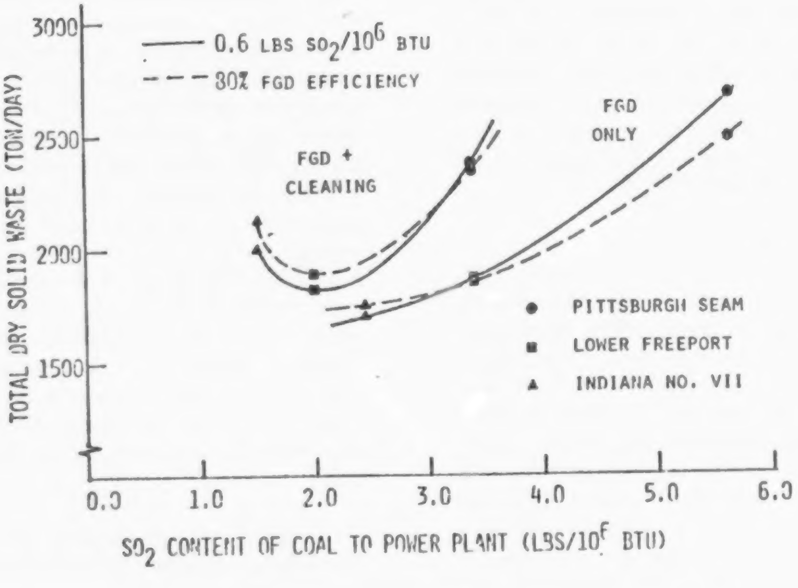


Figure 17. Effect of SO_2 emission regulation on total solid waste generation for three eastern coals (1000 MW net)

rigorous comparisons with a conventional steam-electric plant it is illustrative to examine the environmental consequences implied by typical current designs. Table 9 shows the effect of component energy penalties on the net cycle heat rates for two conventional systems and two gasification system designs. For the gasification system the "best case" design assumes that all steam and electrical requirements needed for desulfurization and wastewater treatment are supplied by recovery or use of waste heat. The "worst case" design assumes that no waste heat can be economically utilized so that all steam and electricity requirements for environmental control systems incur an energy penalty that requires additional coal input to maintain the same net plant output. The wide bounds suggest the

TABLE 9

EFFECT OF SYSTEM ENERGY PENALTIES ON NET CYCLE HEAT RATE FOR A PLANT PRODUCING 1000 MW NET OUTPUT

(Btu per KWH)

(Assuming Pittsburgh Seam Coal and 0.6 lbs $SO_2/10^6$ Btu Coal Input)

System or Component	Conv. Plant w/Limestone FGD	Conv. Plant w/cleaning & FGD	Current Gasification/Comb. Cycle	
			Best Case[a]	Worst Case[b]
Electric Power Generation	8,980	8,980	7,795	8,365
Coal Mining Equipment	55	60	55	75
Coal Preparation:				
Equipment	0	55	95	130
Coal Refuse	0	715	0	0
Primary Coal Pulverizer	25	15	–	–
Coal Gasifier[c]	–	–	2,440	3,175
Flyash Collection	20	20	10	20
Sulfur Removal & Recovery System[d]	345	300	165	1,515
Water Cooling and Treatment[e]	195	190	70	795
Net Cycle Heat Rates:				
Based on coal energy mined	9,620	10,220	10,630	14,075
Based on coal input to plant	9,565	9,505	10,575	14,000
Based on fuel gas from gasifier	n/a	n/a	8,190	11,315

[a] Assumes all energy for desulfurization and wastewater systems is supplied using waste heat.

[b] Assumes all energy for desulfurization and wastewater systems incurs a penalty requiring additional coal input.

[c] Modeled after Bureau of Mines air-blown stirred bed gasifier.

[d] For conventional plant, includes limestone FGD system and its auxiliaries. For gasification plant, includes Benfield acid gas removal, Claus recovery plant and Wellman-Lord tailgas plant.

[e] Includes cooling tower penalty for all Rankine power cycles, plus ammonia recovery, H_2S stripping and biological oxidation for gasification plant.

sizable impact that environmental control system design and performance could have on the viability and environmental impact of gasification-based technologies. If efficient designs can indeed be implemented the overall efficiency of current gasification/combined cycle technologies comes quite close to that of conventional systems (based on coal energy input to the plant). If current designs cannot be realized, gasification is far less efficient than conventional practice. Table 9 suggests that other perspectives of the cycle thermal efficiency are also possible depending on how one chooses to define the "system."

In terms of environmental impact, comparisons between gasification and conventional technologies will depend significantly on future regulatory policy. If coal gasification cycles are subject to the same standards now applicable to direct coal-fired plants the SO_2 mass emissions will depend on the net cycle heat rate (thermal efficiency) based on coal energy input. Figure 18 shows that the current NSPS would result in higher SO_2 emissions using present gasification technology, which is less efficient than conventional technology. Lower emissions would result with future, more efficient designs. On the other hand, if best available control technology must be used, even current gasification processes would achieve lower SO_2 emissions than conventional plants using FGD. TSP emissions would also be virtually eliminated, as it must be to prevent turbine blade erosion. NO_x levels would be less than half current NSPS limits for coal-fired boilers if gas-fired standards could be achieved. However, there is considerable uncertainty about NO_x emissions; they may well be as large or larger than from present coal-fired plants.(9) Finally, less efficient processes will also incur increased coal mining and associated solid waste generation impacts described earlier.

ANALYSIS OF CROSS-MEDIA TRADEOFFS

Given an ability to characterize environmental effluents from different regulatory strategies, the key issue becomes one of defining the levels that are acceptable in light of the tradeoffs that are known to occur. To do this rigorously (Figure 1) requires considerably more knowledge than we have today concerning the transport and transformation of pollutants in the environment and their resulting effects on human health and the ecology. Clearly, more scientific research is needed to provide a stronger basis for policy decisions.

Development of regulations and standards, however, has seldom been hampered by a lack of scientific knowledge. Where data are lacking, personal and societal value judgments play an increasingly important part in public policy. These reflect people's concerns and perceptions regarding levels of environmental risk, economic costs, aesthetic values, political judgments and other concerns that are not often articulated in the development of environmental policy. One aspect of the CMU research on cross-media impacts and tradeoffs concerns the development of methodologies that incorporate both scientific and nonscientific criteria. Two approaches are currently being explored.

Weighted Emissions Inventory

One approach being pursued involves the use of subjective and objective weighting factors for pollutant species and environmental media. This approach was devised by Reiquam, et al., at Battelle Memorial Institute(16) and yields a numerical parameter called the Environmental Degradation Index (EDI). This weighted inventory technique was refined by Dunlap and McMichael at CMU to explicitly display the consequences of alternative values and scientific judgments.(17) The result is a "strategy preference plot," illustrated in Figure 19 for an industrial wastewater control problem. Following the Battelle methodology, the EDI varies with judgments as to the relative importance of air, land, and water as a depository for wastes (reflected by an allocation of 1,000 points). Assumptions regarding the relative damage of pollutant emissions are also incorporated into this methodology. The important point is that when sensitivity analyses are used to explore a wide range of uncertainty in the value of key parameters, the conclusion repeatedly reached for this particular problem is that an intermediate rather than a high level of control is

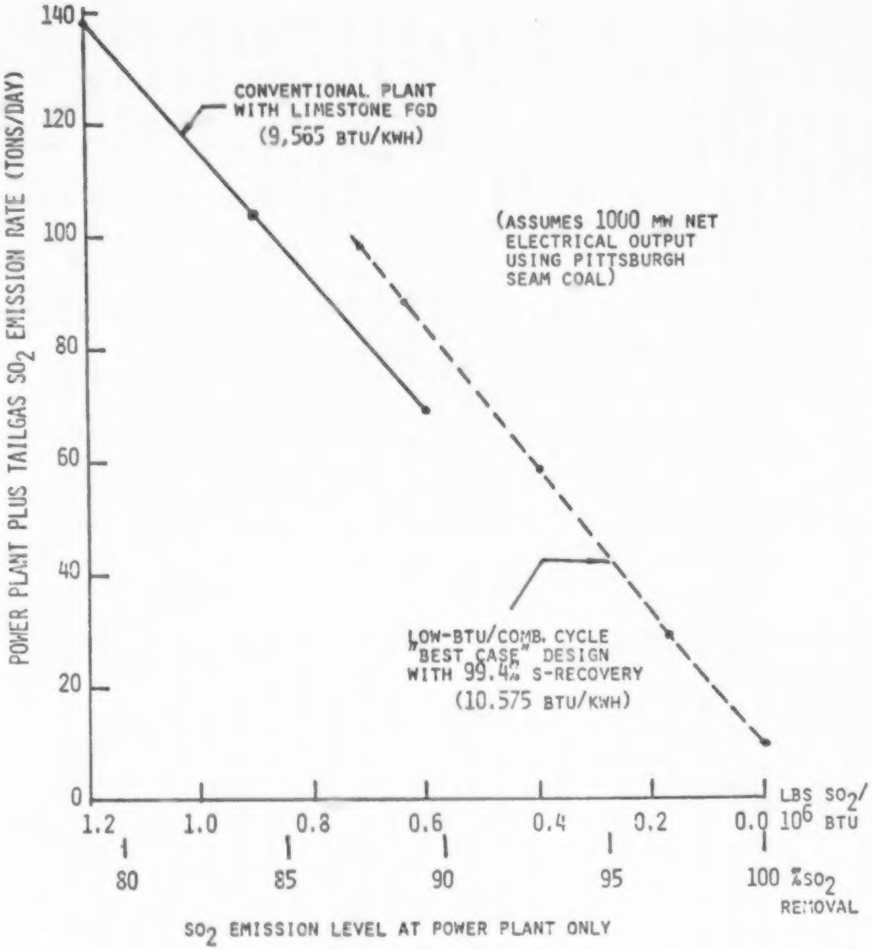


Figure 18. Comparison of SO_2 emissions from present conventional and low Btu/combined cycle plants.

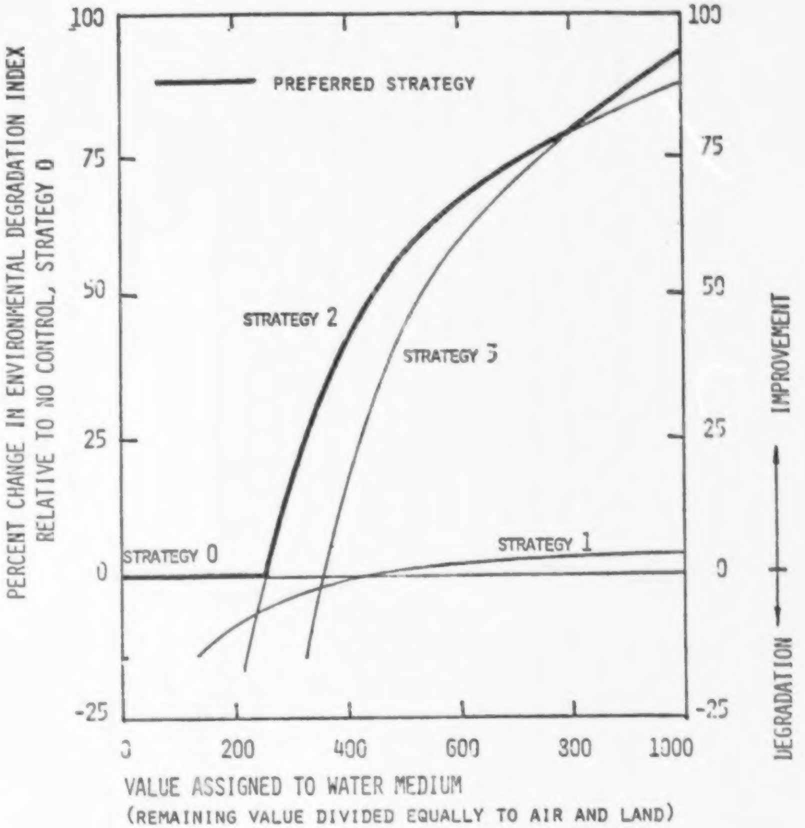


Figure 19. Strategy preference plot for an industrial wastewater problem.

the optimal strategy for minimizing environmental degradation. This is in contrast to current regulatory policy which requiries the highest level of control for wastewater constituents, but ignores the substantial negative impacts on other enviornmental media that are introduced. Articulation of such tradeoffs and their relationship to value judgments is an important step in developing regulatory policies that are in the best interests of overall environmental quality.

Multi-Attribute Utility Theory

Recently we have also begun to examine the applicability of multi-attribute utility theory (MAUT) to the cross-media problem. This refers to a quantitative body of theory developed during the past decade that addresses the problem of making decisions to complex problems when there are multiple desirable objectives, all of which are not simultaneously obtainable. Practical applications of this theory have been relatively limited but have proved useful in the identification of policy tradeoffs into other types of problems.(18-20) The application of MAUT to cross-media analysis is in the explicit preference characterization for different levels of selected pollutants reaching different environmental media. To date, such preferences have either been mandated by law (e.g., new source standards and ambient quality standards) or have been decided on a case-by-case basis. Disagreement over preferences have usually revolved around the relative importance of multiple specific goals. In power plant siting issues, for example, there is little disagreement that reduction of adverse environmental impacts is a worthwhile goal; rather, there is disagreement as to how much reduction is appropriate in light of expected adverse impacts and other nonenvironmental considerations.

Multi-attribute utility theory provides a framework which can explicitly describe the values or preferences of different groups or individuals, indicating where and by how much they differ. From this clearer understanding the magnitude of differences can frequently be reduced during further discussions to arrive at optimal decisions. Implementation of MAUT involves a structured interview/questionnaire with "decision-makers" from various parties as interest. At CMU, preliminary research has been conducted with representatives of electric utility companies, state environmental control agencies, and local citizen groups treating the cross-media problem in the context of siting a new coal-fired power plant. Focusing on tradeoffs among SO_2, heat and particulates to air, ash and FGD sludge to land, and heat to water, this preliminary work showed that the "utility functions" (quantitative value system) of these groups could indeed be characterized using the interview format that was devised. This work remains in progress and will be reported on at a future time.

CONCLUSION

The environmental impact of coal utilization technologies is a complex function of process design, coal properties, and environmental control technology. Regulatory policy for environmental control is a key element in this equation. Historically, regulations and standards limiting the emission of pollutants to air, land, and water have been promulgated without rigorous analysis of the secondary impacts and cross-media effects that adversely influence environmental quality. This paper has described an approach being developed at Carnegie-Mellon University to systematically address such issues as they apply to conventional and advanced technologies producing electricity from coal. Illustrations showed the effect of different SO_2 constraints on the secondary production of pollutants that offset the improvements due to SO_2 reduction alone. Preliminary comparisons of conventional plants and gasification/combined cycle systems were also given. The continuing focus is on careful assessment of the system residuals emitted to various environmental media as a function of process design, coal characteristics, environmental control technology, and environmental regulatory policy. Future efforts will couple this with a cross-media analysis incorporating value judgments and economics to provide greater insight as to the nature of optimal environmental regulatory policy for coal utilization technologies.

ACKNOWLEDGMENTS

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Session III: CONTROL TECHNOLOGY DEVELOPMENT

A. G. Sliger
Chairman

SELECTION OF ACID GAS TREATING PROCESSES FOR COAL CONVERTER OUTPUTS

S. E. Stover and F. D. Hoffert
Hydrocarbon Research, Inc.
Research and Development Division
Lawrence Township, New Jersey 08648

Abstract

Many factors must be evaluated in the selection of acid gas removal processes for coal-derived converter output gases. Some of these considerations, among others, include the gasification process, the sulfur content of the coal, the presence of other contaminants and their effects, the end use of the product, and the multitude of clean-up processes and their economics. While the limited scope of this paper will not permit an in-depth examination of such a complex subject, some generalization will be discussed and applied to some typical cases. One aspect to be discussed is the influence of the sulfur content of coal on the selection process for different converter systems. Typical situations to be examined include a high pressure (1000 psi) case for SNG, an intermediate pressure (400 psi) case for turbine fuel, and a low pressure (atmospheric pressure or slightly above) for industrial fuel.

Generalization for the selection of acid gas treating processes on coal converter output gases is not easily made. Many different factors must be evaluated in order to select from an expanding list of available acid gas removal processes. It will only be possible to examine a few of these aspects within the limited scope of this paper.

One of the most important factors, the sulfur content of coal, provides a starting point for this discussion. Sulfur reports to the output gas primarily as H_2S almost proportionately to its content in coal. The particular process used for gasification of the coal has a relatively minor influence.

In contrast, the carbon dioxide content of gas is greatly dependent on the gasification system. A generalized gasifier performance chart illustrating the carbon dioxide fraction of carbonaceous product gases as a function of H_2/CO ratio is given in Figure 1. In some cases, reactions like the water gas reaction, combustion and methanation proceed further and contribute to variation in product composition.

The difference in the way that sulfur and carbon report is significant because the H_2S/CO_2 ratio and the carbon dioxide partial pressure in the converter output gas is relevant to acid gas removal process selection. Solution oxidation processes such as Stretford or Takahax, which remove H_2S and convert it directly to sulfur, require a high pH in the absorbent solution. High CO_2 concentration lowers the solution pH, and in turn, the rate of H_2S mass transfer in the Stretford solution. As a result, many Stretford process absorbers have ended up being extremely large towers to compensate for low mass transfer rates. The Holmes version of the Stretford process uses an improved gas-solution contacting technique, but even so, high CO_2 concentrations must still be considered carefully when using this process.

The general practice of industry for bulk acid gas clean-up has been to absorb the acid gas from the product gas, convert the H_2S to sulfur by the Claus process and now, to meet environmental demands, clean-up the Claus tail gas with a third process. To become the favored method for bulk acid gas clean up, the selected step-wise approach was undoubtedly governed by economics, and the effect of the gas on solution pH certainly was a contributing factor. Because the Claus process has been so important in most acid gas removal schemes, the influence of sulfur in coal and converter output on the Claus process must be factored into the selection of acid gas removal processes.

Let's look at some typical converter output gas compositions in Table 1. A general, but perhaps not all inclusive, range of gas compositions from low to high CO_2 contents are shown for both oxygen and air blown converters. The data is presented on a dry and sulfur-free basis. Bi-Gas and Wilputte data have been included for later use.

A stoichiometric conversion of sulfur in coal to H_2S in the output gas may be used to develop an equation for an H_2S/CO_2 ratio in the raw product gas as a function of percent sulfur

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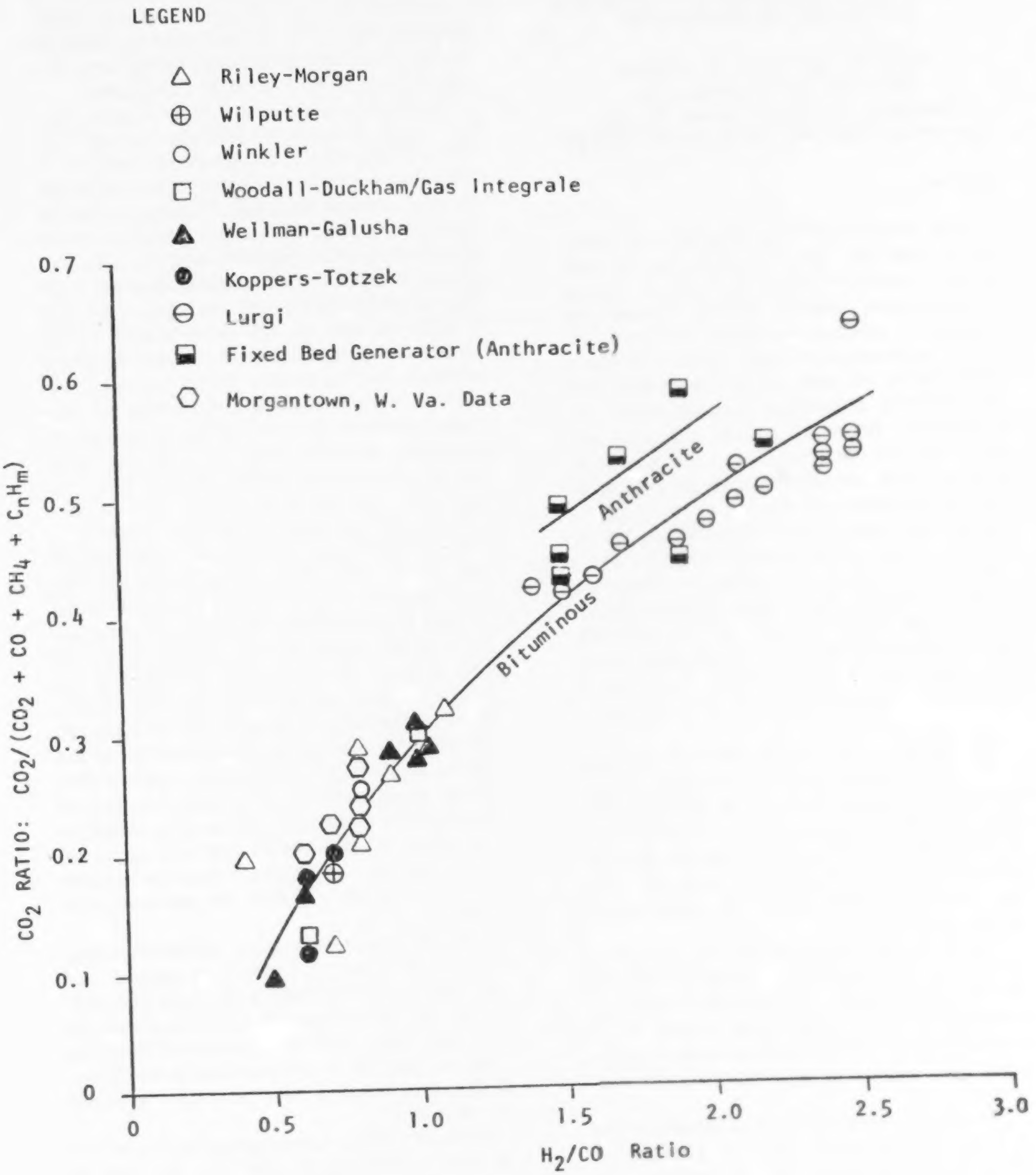

Figure 1. Generalized performance of gasifiers.

TABLE 1

TYPICAL CONVERTER OUTPUT GAS COMPOSITIONS

	OXYGEN BLOWN PROCESSES			AIR BLOWN PROCESS		
DATA SOURCE	KOPPERS -TOTZEK	BI-GAS	LURGI	WELLMAN-GALUSHA	WILPUTTE	LURGI
CO_2 CONTENT	LOW		HIGH	LOW		HIGH
COMPONENTS, VOL.%						
CO_2	7	22	32	3	6	15
CO	57	29	17	29	23	15
H_2	35	32	40	15	17	24
N_2	1	1	1	50	50	40
CH_4	--	16	10	3	4	6

BASIS: DRY AND SULFUR-FREE GAS

in coal. This ratio designated by the letter Y in Table 2 will later be used to provide a guide for determining the need for selective H_2S removal. To correct for losses to other sulfur outlets such as tar or ash, a correction factor, S_r, has been applied. The conversion efficiency, E, used by the equation is the percent of output gas Btu content divided by the Btu content of the process coal. For simplicity, the sulfur recovery and efficiency factors have been arbitrarily set at values of 100 and 75 in the remaining discussion. A sample calculation for a 5 percent sulfur coal is also shown in Table 2.

In Figure 2, a plot of the H_2S ratio versus percent sulfur in coal has been made using points calculated from the H_2S/CO_2 ratio equation as boundary lines. Data taken from actual gasifier operation have been plotted to support the theoretical analysis. Note that the Koppers-Totzek points fall just about on the upper line. The other data points fall within the general area of these arbitrary boundaries to form a typical area of operation.

Two horizontal lines equivalent to 10 and 15 percent H_2S in acid gas have been incorporated on the H_2S ratio graph in Figure 3. These values[1] were chosen because the economic use of the Claus process probably becomes marginal at about this range. One point evident from this chart is that selective absorption of H_2S will, in many cases, be necessary when using the Claus process. Physical solvents are well known for their selective absorption capabilities and will, consequently, find appropriate applications in coal gasification. Some chemical solvents do have some selective absorption capability and this aspect will have to be taken carefully into account in coal gasification applications.

Now let's take a few coal gasification cases and examine what might be considered in the selection of acid gas removal processes. As might be expected, it will not be possible to present a cookbook approach to an undisputed choice for acid gas removal, but some points to be taken into account will be covered including selections using a recently published guideline.[2] The cases which were made to represent typical future situations are:

I. Coal gasification at the 1000 psi level for SNG manufacture and shown in Tables 3 and 4.
II. Coal gasification at the 400 psi level for turbine fuel and shown in Tables 5 and 6.
III. Coal gasification just above atmospheric pressure for industrial fuels and shown in Tables 7 and 8.

Process recommendations which were illustrated in Tables 4, 6, and 8 were physical solvent acid removal processes for the two high pressure cases and a chemical conversion process for the low pressure application. The major missing ingredient in this discussion is comparative economics. The reason is that this information is so difficult to obtain and has such a fragile nature when available. It depends so much on the specifics of the particular application, the environmental constraints, the periods of time and even individual discretion in process and cost estimation. However, some guidelines have been demonstrated and, in particular, a look at the estimated acid gas composition from coal and its impact on process selection has been illustrated by examples.

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TABLE 2

SULFUR RATIO IN CONVERTER OUTPUT GAS

AN EQUATION FOR THE RATIO OF HYDROGEN SULFIDE TO CARBON DIOXIDE IN CONVERTER OUTPUT GAS IS:

$$Y = 11.82 \left(\frac{Sc \quad Sr \quad Hg}{C \quad E \quad Hc}\right)$$

WHERE:

Y = H_2S TO CO_2 RATIO IN RAW OUTPUT GAS

Sc = PERCENT BY WEIGHT SULFUR IN COAL

Sr = PERCENT SULFUR REPORTING TO OUTPUT GAS

Hg = HIGH HEATING VALUE OF THE OUTPUT GAS

C = PERCENT BY VOLUME CO_2 IN OUTPUT GAS

E = COAL TO GAS PERCENT EFFICIENCY

Hc = HIGH HEATING VALUE OF THE COAL

ASSUMPTION: ALL SULFUR IN OUTPUT GAS AS H_2S

EXAMPLE CALCULATION:

$$Y = 11.82 \left(\frac{5.0 \times 100 \times 300}{7 \times 75 \times 12{,}000}\right) = 0.281$$

H_2S/CO_2 Ratio

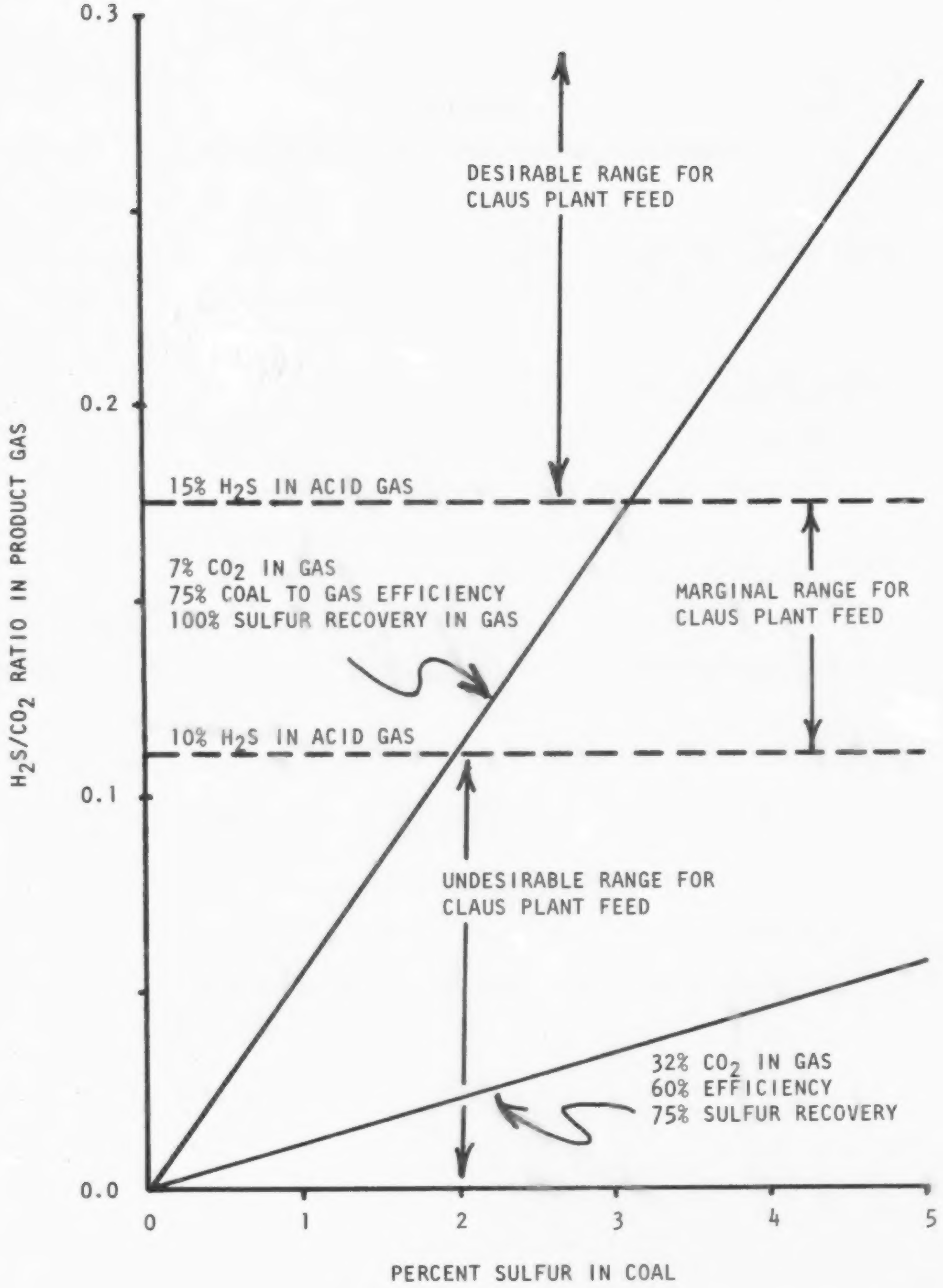

Figure 3. Sulfur transfer to gas in coal gasification.

TABLE 3

EXAMPLE I — GAS REMOVAL SELECTION FACTORS

STUDY BASIS:	CONVERTER	PRESSURE	SULFUR IN COAL	END USE
	BI-GAS	~1000 PSI	4%	SNG

GENERAL CONSIDERATIONS

- ° LOW LEVELS OF H_2S AND CO_2 ARE REQUIRED
- ° CONSERVATION OF GAS HEAT CONTENT IS DESIRABLE

STRETFORD PROCESS CONSIDERATIONS

- ° CONVERTER OUTPUT CO_2 IS 22% OR ~200 PSI PARTIAL PRESSURE
- ° CO_2 PARTIAL PRESSURE IS TOO HIGH

CLAUS PROCESS CONSIDERATIONS

$$Y = 11.82 \left(\frac{Sc}{C} \; \frac{Sr}{E} \; \frac{Hg}{Hc} \right) = \frac{11.82 \times 4 \times 100 \times 360}{22 \times 75 \times 12{,}000} = 0.086$$

- ° H_2S PARTIAL PRESSURE IN PRODUCT GAS = ~20 PSI
- ° H_2S PERCENT OF TOTAL ACID GAS = 8%
- ° SELECTIVE ABSORPTION IS REQUIRED FOR CLAUS ECONOMY

TABLE 4

EXAMPLE I – ACID REMOVAL PROCESS RECOMMENDATIONS

STUDY BASIS:	CONVERTER	PRESSURE	SULFUR IN COAL	END USE
	BI-GAS	$\sim$1000 PSI	4%	SNG

GUIDELINE[2] CHOICES

- SIMULTANEOUS REMOVAL OF H_2S AND CO_2

  ABOVE 75 PSI ACID GAS PRESSURE IN FEED AND BELOW 1 PSI ACID GAS PRESSURE IN PRODUCT - ECONOMINE, HIGH LOADING DEA OR SELEXOL

- SELECTIVE H_2S REMOVAL IN PRESENCE OF CO_2

  3 TO 60 PSI H_2S PRESSURE - ADIP
  ABOVE 60 PSI H_2S PRESSURE - RECTISOL OR SELEXOL

- COMMENT: USE SELECTIVE ABSORPTION TO IMPROVE CLAUS FEED

SPECIAL CONSIDERATIONS (COAL DERIVED GAS PROCESSED TO SNG)

- ADIP - PARTICULATES, TARS AND OILS CAN CAUSE FOAMING
  - CS_2, MERCAPTANS, COS CAUSE SOLVENT LOSSES

- RECTISOL - APPLIED AT SASOL PLANT
  - REMOVES COS, CS_2 AND HCN
  - REFRIGERATION: EXPENSIVE AND HEAT LOSSES

- SELEXOL - SOLVENT NOT DEGRADED BY IMPRUITIES
  - REMOVES SOME COS, CS_2, NH_3 AND HCN

RECOMMENDATIONS

- SELEXOL WOULD BE A GOOD SELECTION AND IT HAS BEEN CHOSEN FOR BI-GAS PILOT PLANT AT HOMER CITY

- FINAL DECIDING FACTOR DEPENDS ON ECONOMICS AND TEST RESULTS

TABLE 5

EXAMPLE II – ACID GAS REMOVAL SELECTION FACTORS

	CONVERTER	PRESSURE	SULFUR IN COAL	END USE
STUDY BASIS:	AIR BLOWN LURGI	~400 PSI	4%	TURBINE FUEL

GENERAL CONSIDERATIONS

- SULFUR REMOVAL REQUIREMENTS LESS STRINGENT THAN FOR SNG
- CONSERVATION OF GAS HEAT CONTENT IS DESIRABLE
- CO_2 REMOVAL IS UNDESIRABLE

STRETFORD PROCESS CONSIDERATIONS

- CONVERTER OUTPUT CO_2 IS 15% OR ~60 PSI PARTIAL PRESSURE
- CO_2 PARTIAL PRESSURE IS PROBABLY TOO HIGH
- LOWER HEAT EFFICIENCY THAN HIGH TEMPERATURE PROCESSES

HIGH TEMPERATURE PROCESS CONSIDERATIONS

- FRODINGHAM AND OTHER DRY IRON OXIDE PROCESSES
  - UNDER DEVELOPMENT OR NOT YET PROVEN
  - SO_2 BY-PRODUCT
- HOT CARBONATE PROCESS
  - ALKALI METAL CARRY-OVER IS VERY DAMAGING TO TURBINE
  - BEING TESTED FOR THIS APPLICATION AT POWERTON PLANT IN ILLINOIS

CLAUS PROCESS CONSIDERATIONS

$$Y = 11.82\left(\frac{Sc\quad Sr\quad Hg}{C\quad E\quad Hc}\right) = \frac{11.82 \times 4 \times 100 \times 180}{15 \times 75 \times 12{,}000} = 0.063$$

- H_2S PARTIAL PRESSURE IN PRODUCT GAS = ~4 PSI
- H_2S PERCENT OF TOTAL ACID GAS = 6%

TABLE 6

EXAMPLE II – ACID GAS REMOVAL PROCESS RECOMMENDATIONS

STUDY BASIS:	CONVERTER	PRESSURE	SULFUR IN COAL	END USE
	AIR BLOWN LURGI	$\sim$400 PSI	4%	TURBINE FUEL

GUIDELINE[2] CHOICES

° SELECTIVE H_2S REMOVAL IN PRESENCE OF CO_2

3 TO 60 PSI H_2S PRESSURE - ADIP
BELOW 3 PSI H_2S PRESSURE - STRETFORD, VETROCOKE OR ADIP

SPECIAL CONSIDERATIONS (COAL-DERIVED GAS PROCESSED TO TURBINE FUEL)

° ADIP - PARTICULATES, TARS AND OILS CAN CAUSE FOAMING
- CS_2, MERCAPTANS, COS CAUSE SOLVENT LOSSES

° VETROCOKE - CONTAINS ARSENIC AND ALKALI SALTS

° FRODINGHAM - NOT ESTABLISHED AND SO_2 PRODUCT

° HOT CARBONATE - POTENTIAL PROBLEM WITH ALKALI SALT

RECOMMENDATIONS

° PHYSICAL SOLVENT PROCESS

° FINAL DECIDING FACTOR WOULD PROBABLY DEPEND ON ECONOMICS

TABLE 7

EXAMPLE III – ACID GAS REMOVAL SELECTION FACTORS

STUDY BASIS:	CONVERTER	PRESSURE	SULFUR IN COAL	END USE
	WILPUTTE	ABOVE ATMOSPHERIC	4%	INDUSTRIAL FUEL

GENERAL CONSIDERATIONS

° SPECIFIC END USE WILL BE INFLUENTIAL

° SULFUR REMOVAL REQUIREMENTS LESS STRINGENT THAN FOR SNG

° CO_2 REMOVAL PROBABLY NOT NECESSARY

STRETFORD PROCESS CONSIDERATIONS

° SATISFACTORY FOR LOW H_2S PARTIAL PRESSURES

° SELECTIVELY REMOVES H_2S

° LOW CO_2 PARTIAL PRESSURE IS AVAILABLE

CLAUS PLANT CONSIDERATIONS

$$Y = 11.82 \left(\frac{Sc \quad Sr \quad Hg}{C \quad E \quad Hc} \right) = \frac{11.82 \times 4 \times 100 \times 160}{6 \times 75 \times 12{,}000} = 0.141$$

° H_2S PARTIAL PRESSURE IN PRODUCT GAS = ~0.2 PSI

° H_2S PERCENT OF TOTAL ACID GAS = 12%

° SELECTIVE ABSORPTION SUGGESTED FOR CLAUS ECONOMY

TABLE 8

EXAMPLE III – ACID GAS REMOVAL PROCESS RECOMMENDATIONS

STUDY BASIS:	CONVERTER	PRESSURE	SULFUR IN COAL	END USE
	WILPUTTE	ABOVE ATMOSPHERIC	4%	INDUSTRIAL FUEL

GUIDELINE[2] CHOICES

° SELECTIVE H_2S REMOVAL IN PRESENCE OF CO_2

BELOW 3 PSI H_2S PARTIAL PRESSURE - STRETFORD, VETROCOKE OR ADIP

SPECIAL CONSIDERATIONS (COAL-DERIVED GAS TO INDUSTRIAL FUEL)

°ADIP - PARTICULATES, TARS AND OILS CAN CAUSE FOAMING
- CS_2, MERCAPTANS, COS CAUSE SOLVENT LOSSES

° VETROCOKE - CONTAINS ARSENIC

° STRETFORD: ADDITIONAL POINTS FOR THE APPLICATION

- PREVIOUSLY APPLIED TO COAL DERIVED GASES
- NITROGEN COMPOUNDS, IF TOO HIGH TO BE TOLERATED, CAN BE REMOVED BY PRETREATMENT
- MAKES ELEMENTAL SULFUR

RECOMMENDATION

° SOLUTION OXIDATION PROCESS SUCH AS STRETFORD

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A COAL GASIFICATION — GAS CLEANING TEST FACILITY

J. K. Ferrell, R. M. Felder,
R. W. Rousseau, D. W. Alexander
North Carolina State University
Department of Chemical Engineering
Raleigh, North Carolina 27607

Abstract

A general purpose coal gasification - gas cleaning facility is being constructed at North Carolina State University for research on effluents from coal gasification processes. The facility consists of a continuous, fluidized bed gasifier; a particulates, condensables, and solubles removal system; and an acid gas removal system. The gasifier operates at pressures up to 100 psig, has a capacity of 50 pounds of coal per hour, and can be run with either air or oxygen. The acid gas removal system is modular in design so that alternative absorption processes can be studied.

The facility is described in detail, the objectives of the research program are outlined, and details of the experimental plan are presented.

INTRODUCTION

Methods to gasify coal and to purify the resulting synthesis gas have been available for decades; several dozen commercial gasification processes are currently operable, and many more are in advanced developmental stages. At present, however, there is still inadequate knowledge of the environmental effects associated with the widespread large-scale implementation of coal gasification technology.

In recognition of this problem, the Environmental Protection Agency has contracted for the construction of a pilot plant coal gasification-gas cleaning test facility at North Carolina State University, to be operated by faculty and staff of the Department of Chemical Engineering. The facility consists of a continuous fluidized bed gasifier, a system for removing particulates, condensables, and soluble matter (PCS) from the raw synthesis gas, and an acid gas removal system (AGRS). The gasifier operates at pressures up to 100 psig, has a capacity of 50 lb coal/hr, and can run with either steam -O_2 or steam-air feed mixtures. The AGRS is modular in design, so that alternative absorption processes may be evaluated with a minimal amount of system modification being required.

The overall objective of the project is to characterize completely the gaseous and condensed phase emissions from the gasification-gas cleaning process, and to determine how emission rates of various pollutants and methanation catalyst poisons depend on adjustable process parameters.

Specific tasks to be performed are as follows:

1. Identify and measure the gross and trace species concentrations in the gasifier product, including concentrations of sulfur gases (H_2S, COS), condensable organics (e.g. BTX and polynuclear aromatic hydrocarbons), water-soluble species (e.g. ammonia, cyanates, cyanides, halides, phenols, sulfates, sulfides, sulfites, and thiocyanates), and trace metals (e.g. antimony, arsenic, beryllium, bismuth, cadmium, lead, mercury, selenium, and vanadium).
2. Correlate measured emission levels with coal composition and gasifier operating variables, particularly temperature, pressure, and solid and gas phase residence time distributions.
3. Perform material balances around the gasifier, the raw gas cleanup (PCS) system, and the acid gas removal system, and determine the extent to which selected species are removed from the synthesis gas in each of the components.
4. Correlate measured removal efficiencies for various species with system operating variables, including temperatures, pressures, holdup times, and solvent circulation rates.
5. Evaluate and compare the performance characteristics of alternative acid gas removal processes, considering both CO_2 and H_2S removal capabilities and the degrees to which the processes remove trace pollutant species from the sour synthesis gas. Evaluate the

buildup of contaminates in the various acid gas removal solvents.

6. Use the results obtained in the above studies to develop models for the gasification and the gas cleanup processes. The models will take as input variables the composition and feed rate of the coal, bed depth, steam and air (or oxygen) feed rates and inlet temperatures, gasifier pressure, and operating conditions (temperatures, pressures, solvent flow rates, etc.) for the gas cleaning systems, and will predict the coal conversion and the product gas flow rate and composition, including trace pollutant levels. The model will be used as a basis for optimizing the pilot plant operating conditions, and for estimating emission levels for scaled-up versions of the processes investigated.

The sections that follow will present a brief description of the facility, the experimental program, and methods of analysis.

THE FACILITY

A sketch of the pilot plant facility is shown in Figure 1. The sketch is approximately to scale and shows the location of the major components of the plant and the important piping. Although no scale is indicated on the figure, the acid gas stripping column is the tallest unit and is approximately 13.5 meters (44 feet) in height.

The facility can be divided into nine subsystems as listed below:

1. Gasifier, Coal Feed, and Char Handling
2. Particulates, Condensibles, and Solubles Removal (Raw gas cleaning)
3. Acid Gas Removal
4. Product and By-Product Disposal
5. Sampling and Analysis
6. Measurement and Control
7. Safety
8. Synthetic Gas Mixture
9. Support

Only Items 1, 2, and 3 will be described in any detail here.

Schematic diagrams of the system are shown in Figures 2 and 3 and a drawing of the gasifier is shown in Figure 4. The gasifier is a fluidized bed unit and was designed by personnel at the Illinois Institute of Gas Technology; it is essentially a copy of a gasifier now in operation at IGT. Although the gasifier, coal feed hopper and char receiver vessels are designed for much higher pressures, the remainder of the system limits the operation of the gasifier - PCS system to approximately 100 psig.

The internal dimensions of the gasifier allow fluidized bed dimensions of 6 inches in diameter and up to 5 1/2 feet in height. Coal is fed at the top by a screw feeder from a pressurized coal feed hopper and char is removed from the bottom into a pressurized char receiver. The gasifier is instrumented with a bed height detector, and temperature and pressure sensors are located at several positions within the bed. A preheated air-steam or O_2-steam mixture is introduced into the bottom of the gasifier bed.

The raw gas goes to a cyclone separator for removal of most of the particulates and then to a venturi scrubber where it is cooled and water soluble and condensable compounds are removed. A portion of the effluent is subjected to further cooling and condensate removal, and is then sent to the acid gas removal system.

The AGRS consists of an absorber column for removal of the acid gases, primarily CO_2 and H_2S, and a stripper column for regeneration of the solvent. At least four processes will be studied: refrigerated methanol, hot potassium carbonate, monoethanolamine and Dimethylether of Polyethyleneglycol. Table I shows the operating conditions expected in each process. The first process investigated will use methanol which will also be used for the plant shakedown and startup runs.

For the methanol system the cool, dry sour gas is compressed to 500 psig and fed to the bottom of the absorber column where the CO_2 and H_2S are absorbed. The methanol is introduced into the top of this column at approximately minus 30 degrees Fahrenheit. The acid gases are stripped with nitrogen in the stripper column operating at approximately 15 psig and 0°F. Although the AGRS is not designed to duplicate a commercial system, it has sufficient flexibility to cover the full range of operating parameters applicable to commercial units.

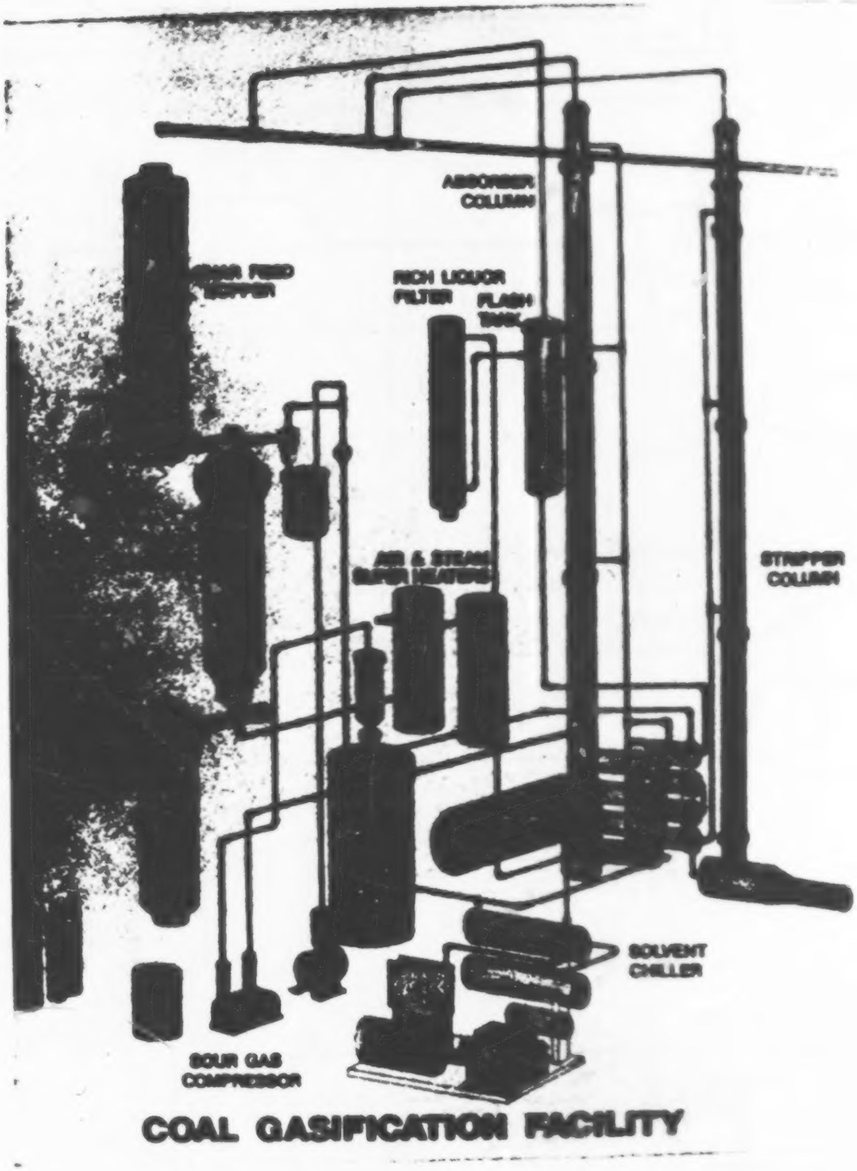
ABSORBER COLUMN
COAL FEED HOPPER
RICH LIQUOR FILTER
FLASH TANK
AIR & STEAM SUPER HEATERS
STRIPPER COLUMN
SOLVENT CHILLER
SOUR GAS COMPRESSOR
COAL GASIFICATION FACILITY

Figure 1

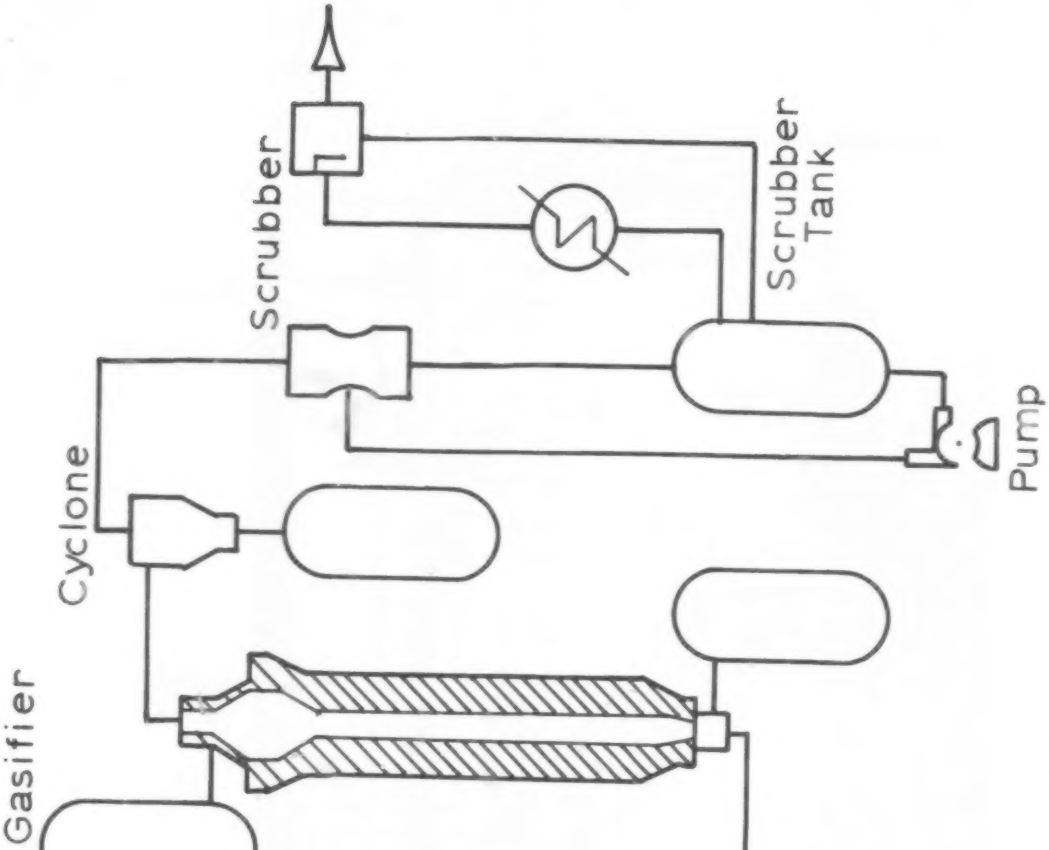
Air
M
Compressor
O_2
N_2
Steam
Preheater
Super Heater
Gasifier
Cyclone
Scrubber
Scrubber Tank
Pump

Figure 2. Gasifier and gas quench system.

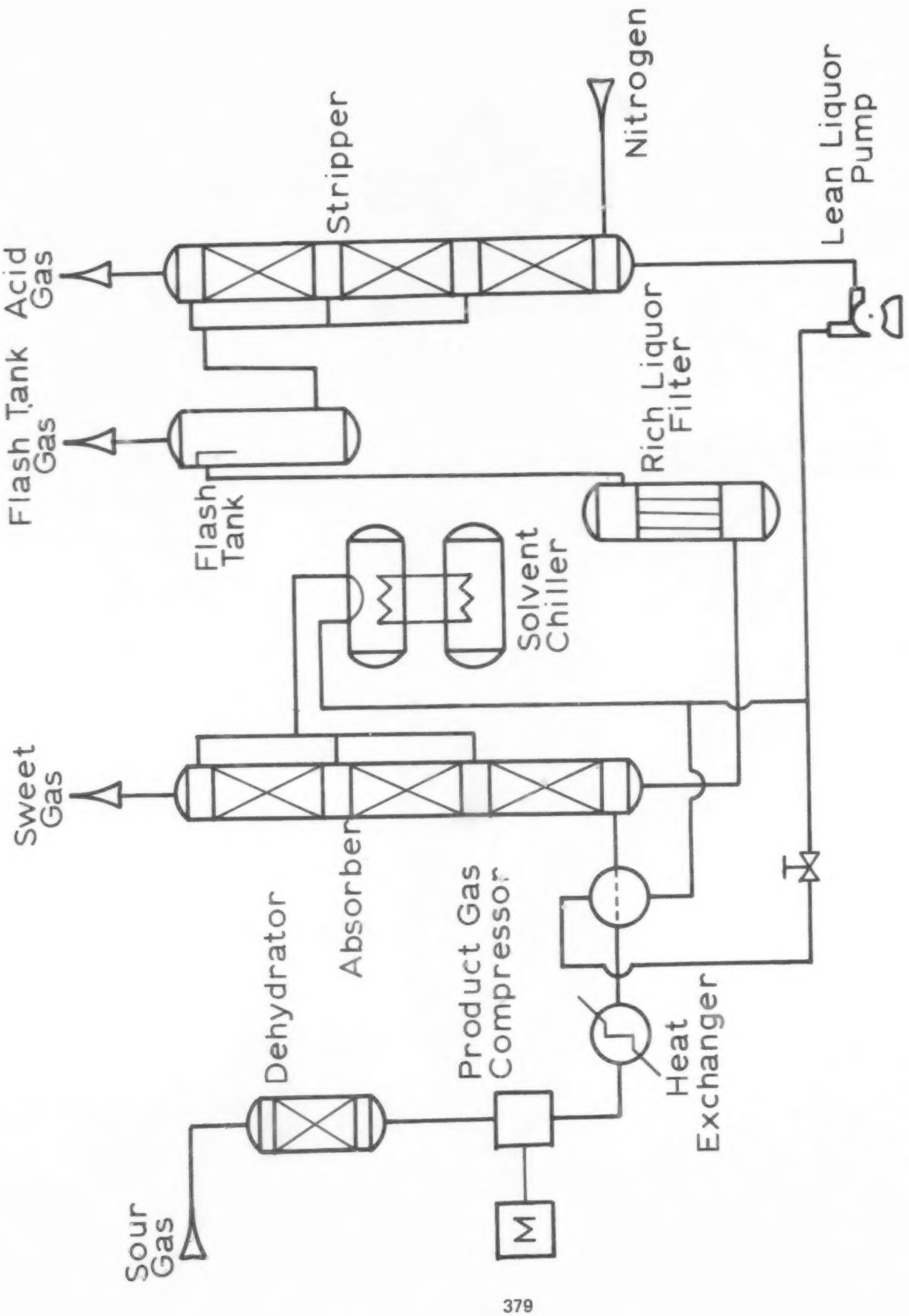
Sour Gas
M
Dehydrator
Product Gas Compressor
Heat Exchanger
Absorber
Sweet Gas
Solvent Chiller
Flash Tank
Flash Tank Gas
Rich Liquor Filter
Acid Gas
Stripper
Nitrogen
Lean Liquor Pump

Figure 3. Acid gas removal system.

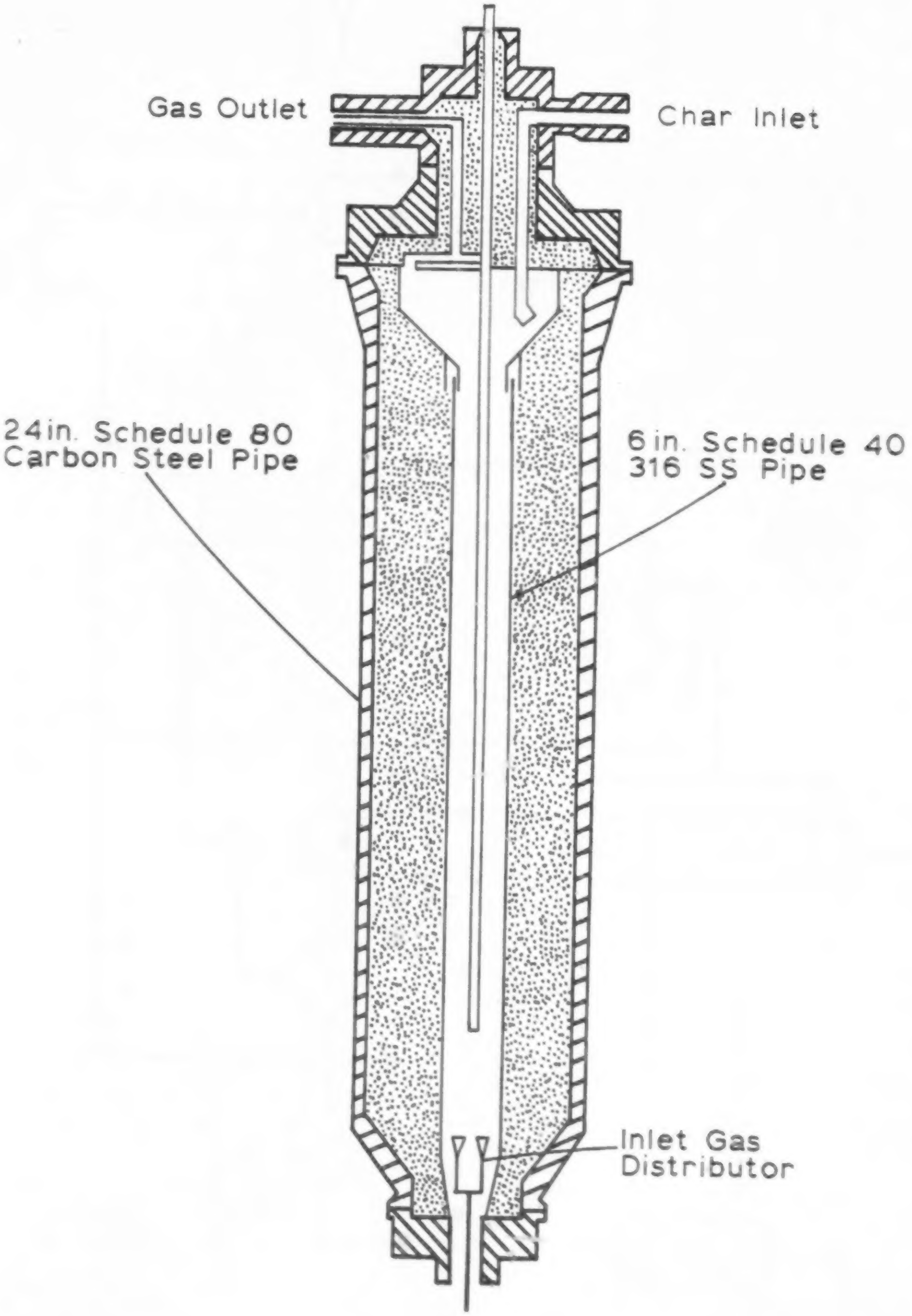
Gas Outlet
Char Inlet
24in. Schedule 80
Carbon Steel Pipe
6in. Schedule 40
316 SS Pipe
Inlet Gas
Distributor

Figure 4. Gasifier cut-away.

TABLE 1

ACID GAS REMOVAL SYSTEM OPERATING CONDITIONS

	Absorber		Stripper		Flash Tank	Composition	
Solvent	Pressure (psia)	Temperature (°F)	Pressure (psia)	Temperature (°F)	Pressure (psia)	Percent CO_2	PPM H_2S
MeOH	315-515	-30	15-45	0	115-215	1.7	700
DMPEG	315-515	20	15-45	30	115-	3.0	500
K_2CO_3	115-315	230	20-55	230	Not Used	0.45	200
MEA	115-315	120	20-55	260	Not Used	Trace	Trace

The excess raw gas, the sweet gas, and the sour gas are recombined and sent to an incinerator for disposal.

The facility is instrumented so that approximately 100 of the process variables, temperatures, pressures, flow rates, and liquid levels, and some chemical compositions are available in real time for the data acquisition system. Process control is implemented by a Honeywell TDC 2000 digital control system.

A schematic diagram of the data acquisition system is shown in Figure 5. The system also has the capability of presenting process variables in engineering units on a real time log for operator information, computing mass flow rates, and performing material and heat balance calculations.

THE EXPERIMENTAL PROGRAM

The experimental program will begin when the facility is turned over to North Carolina State University in the late spring or early summer of 1978.

The first phase of the program will be devoted to testing the acid gas removal system using synthetic feed gas mixtures, and operating the gasifier with a pretreated coal or char feed—first alone, then in combination with the AGRS. At the conclusion of this phase of the program, the following objectives should be achieved:

1. The analytical chemical procedures to measure all gross and trace components of interest will be standardized.
2. Mass transfer coefficients and vapor-liquid equilibrium parameters for the methanol absorption system will be measured, and the CO_2 and H_2S removal capabilities of the system will be determined as functions of the operating temperatures and pressures of the absorber and stripper units. Also measured will be the degree to which the CO and H_2 are removed from the sour synthesis gas, and the rate at which methanol is lost due to entrainment and evaporation.
3. The gasifier startup, operating, and data collection procedures will be standardized.
4. The gross and trace emissions from the gasifier will be measured, and their levels will be correlated with operating conditions. Material balances will be obtained, and the operating characteristics and efficiency of the particulate condensation and scrubbing system will be determined.
5. The operation of the integrated gasifier - gas cleaning system will be tested at several conditions, and the degree to which the system performance can be

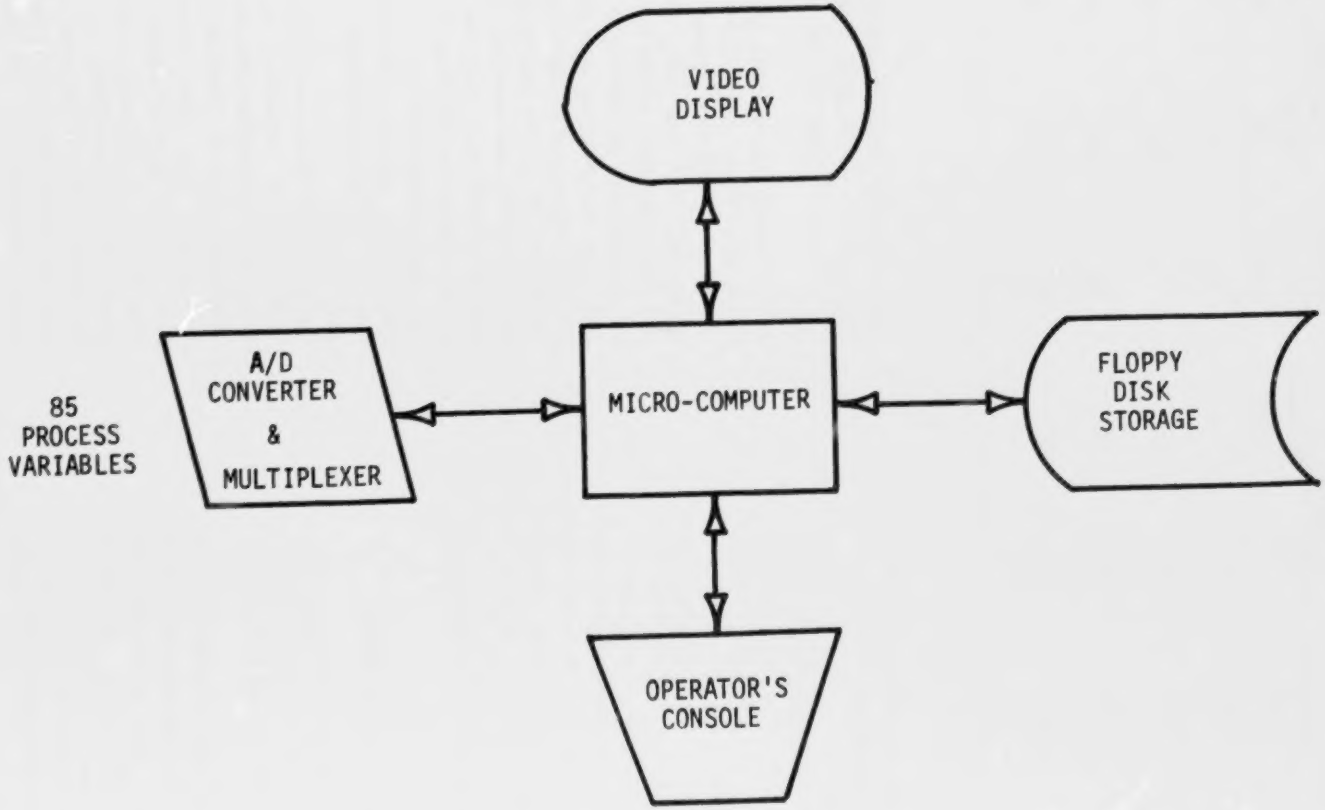
VIDEO DISPLAY
85 PROCESS VARIABLES
A/D CONVERTER & MULTIPLEXER
MICRO-COMPUTER
FLOPPY DISK STORAGE
OPERATOR'S CONSOLE

Figure 5. Schematic of data acquisition system.

predicted from the models and correlations established in the previous studies will be determined.

Upon the completion of these studies, the program will shift to the more difficult task of operating with a non-pretreated, non-caking coal. A detailed experimental plan for this stage of the program will be developed in light of the first-stage results.

During the first week of operation, the complete gasification facility will be pressure tested and inspected for physical integrity. Later, flooding velocities will be determined for the absorber and stripper at anticipated operating pressures.

In the remaining six months detailed experimental work will begin. We will determine CO_2, H_2S, COS, CO, and H_2 transfer rates as functions of absorber and stripper temperatures and pressures, solvent circulation rate, and feed gas inlet temperature. Later the gasifier will be operated using a pretreated char. The emission rates of principal synthesis gas components, sulfur-containing gases, volatile organics, and trace elements will be determined. The emission levels will be correlated with various operating parameters in an attempt to develop predictive emission models. Near the end of the six month period, the gasifier and AGRS system will be operated as an integrated unit. These runs will be used to check the consistency of the results with predictions based on operation of the individual system components.

At least three sets of operating conditions for the gasifier and two sets for the AGRS will be tested in all six possible combinations: the particular conditions will be chosen based on the results of the previous studies.

Sampling

Duplicate grab samples will be obtained from the sampling points shown in Figure 6. The sampling will be done during steady state operation of the pilot plant. Composite sampling will be required for some streams, such as the aqueous condensate obtained from sampling point 7. Gas samples will be taken using a sampling train like that shown in Figure 7.

Analytical Procedures

The various chemical species to be monitored in the gasification unit are shown in Table II. Elemental analyses will be limited to those elements in the first two columns of Table II. The bulk element balances ensure that the entire stream has been accounted for before any other analyses are made. The trace elements selected are those expected to have the most adverse impacts on the environment adjacent to a coal gasification facility.

The water-borne compounds and ions of interest include hazardous species such as cyanide and cyanate, and industrially important species, such as benzene, toluene, xylene, and phenols.

The analysis samples can be classified into four major types:

1. Solid samples - coal, char, and particulates.
2. Aqueous liquid samples - feed water, water condensate, and scrubber water.

TABLE 2

ANALYSES OF INTEREST IN THE COAL GASIFICATION PROCESS

Trace Elements	Bulk Elements	Water-Borne Compounds	Gaseous Compounds
As	C	CN^-	H_2
Be	H	$CNO^=$	H_2
Bi	N	$CNS^=$	CO
Cd	O	Cl^-	CO_2
Hg	S	$S^=$	SO_2
Pb		$SO_3^=$	H_2S
			H_2O
Sb		$SO_4^=$	CH_4
Se		NH_4^+	C_2H_6
V			COS
Cr		Benzene	CH_3OH
		Toluene	
		Zylene	
		Phenols	

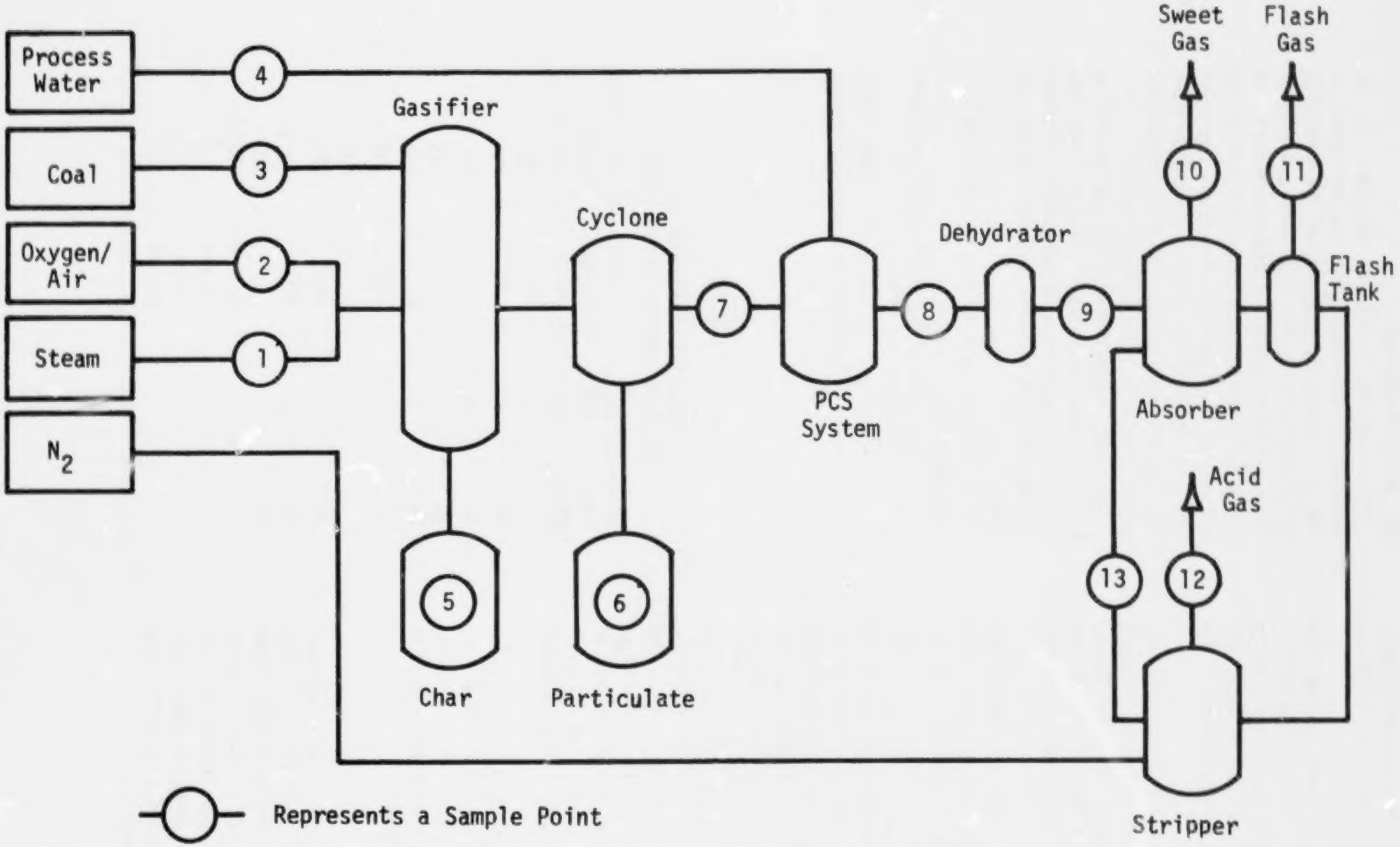
Process Water
Coal
Oxygen/ Air
Steam
N_2
4
3
2
1
Gasifier
Cyclone
7
PCS System
8
Dehydrator
9
Sweet Gas
Flash Gas
10
11
Absorber
Flash Tank
Acid Gas
13
12
Stripper
5
6
Char
Particulate
Represents a Sample Point

Figure 6. Location of sample points.

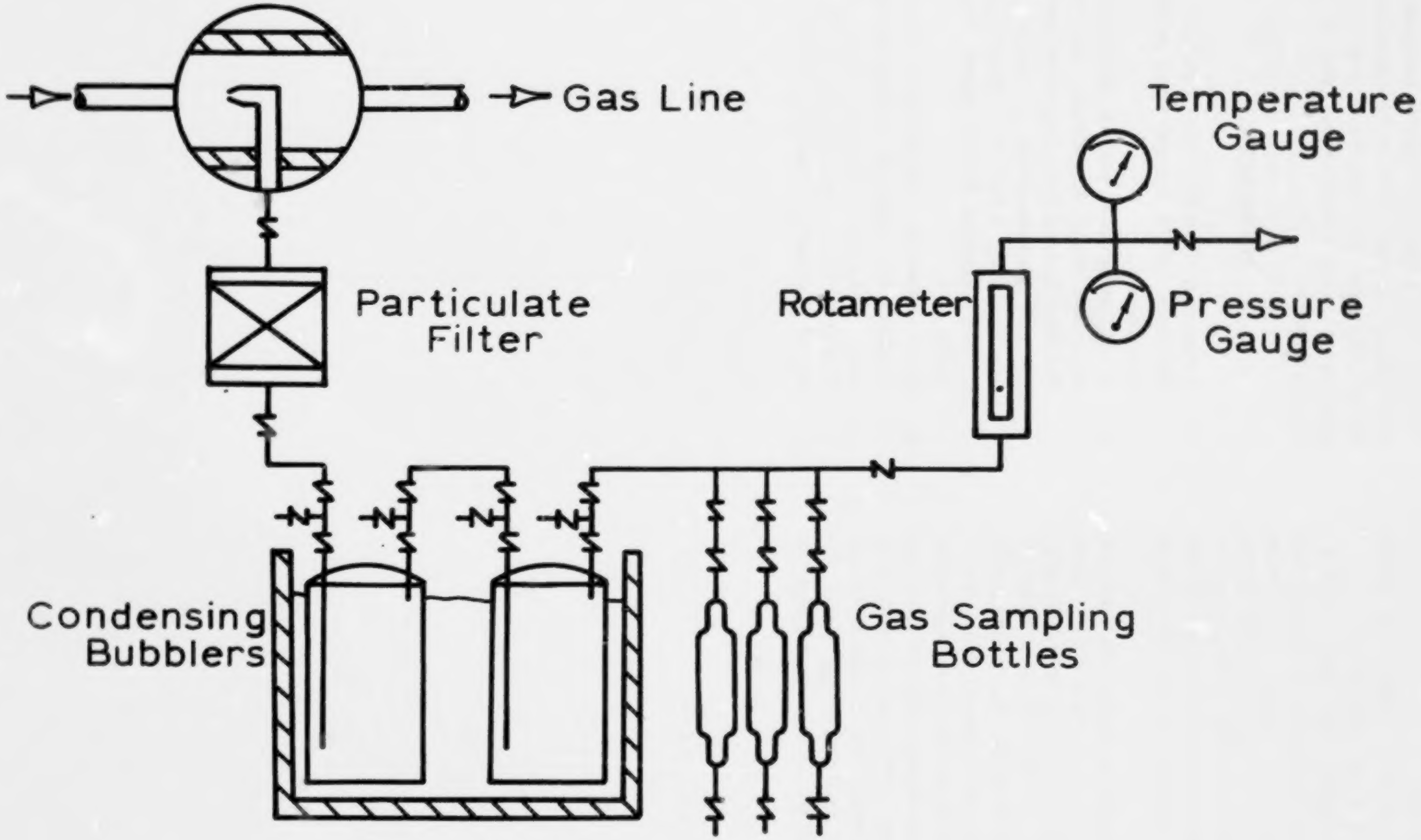
Gas Line
Temperature Gauge
Particulate Filter
Rotameter
Pressure Gauge
Condensing Bubblers
Gas Sampling Bottles

Figure 7. Prototype gas sampling train.

3. Organic liquids - AGRS liquors, organic fraction of tars.
4. Gaseous samples - product gas, sweet gas, flash gas, and acid gas.

Whenever applicable, standard ASTM[1], APHA[2] and EPA[3] methods and procedures will be used initially; more highly automated methods of analysis may be substituted for the manual methods in later stages of the program. The standard methods will then serve to check the accuracy and reliability of the instrumental procedures.

Several instrumental analyses are currently being developed for use in the program. Trace elements will be determined by atomic absorption spectroscopy, neutron activation analysis, and colorimetric procedures. Gas analyses will be performed using gas chromatography. Some water analyses will be performed by atomic absorption spectrophotometry and selective ion electrode methods. Total carbon and total organic carbon in water will be determined using an FID-based instrumental analyzer. Instruments that will be used in later stages of the program include an automated C, H, N, O, S analyzer for solid and liquid samples, an automated titrater, and a microprocessor-based specific ion electrode meter, and possibly a mass spectrometer and a liquid chromatograph.

REFERENCES

1. American Society for Testing and Materials, *1976 Annual Book of ASTM Standards.*
2. American Public Health Association, American Water Association, and Water Pollution Control Fed., *Standard Methods for the Examination of Water and Wastewater,* 14th ed., Washington, D. C., American Public Health Assoc., 1976.
3. Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes,* Report No. EPA 625/6-74-003, Washington, D. C., Office of Technology Transfer, 1974.

CONTROL TECHNOLOGY DEVELOPMENT FOR PRODUCTS/ BY-PRODUCTS OF COAL CONVERSION SYSTEMS

Sohrab M. Hossain, John W. Mitchell,
and Alfred B. Cherry
Catalytic, Inc., Philadelphia, Pennsylvania

Abstract

The objective of developing control technologies for the products and by-products of coal conversion systems is to permit the fullest utilization of these materials while controlling environmental pollution within acceptable levels. Products are defined as the primary marketable materials such as low, medium and high Btu gas; liquefied and solvent refined coal. By-products are all other potentially usable components of coal conversion systems.

Coal gasification and liquefaction processes were studied to establish the expected slate of products and by-products. Most processes produce recoverable quantities of sulfur, ammonia, phenol, naphtha, tars, tar oils, and char by-products. Lower temperature gasification processes produce a wide range of by-products; whereas higher temperature processes produce fewer by-products. The operating pressure of the gasifiers is a secondary variable. Almost all coal liquefaction processes yield a full slate of by-products.

Potential pollutants from products/by-products and their control needs are presented. A number of existing and developing technologies for upgrading by-products and for control of effluents are reviewed. On-going work on environmental data acquisition and control technology assessment are discussed.

INTRODUCTION

The economics and environmental impact of coal liquefaction and gasification systems in the U.S.A. will depend to a large extent on effective recovery and use of by-products. Such coal conversion by-products generally include phenol, tar, ammonia, char, ash, and sulfur.

The U.S. Environmental Protection Agency awarded a three-year contract to Catalytic, Inc. in September, 1976 to conduct a program aimed at development of control technology for the products and by-products of fuel conversion and utilization systems based on coal. This paper outlines the project scope, analyzes the conversion products and by-products and their pollution control needs, and reviews pertinent recovery and pollution control technologies.

For the purpose of this project, the following definitions apply: coal conversion systems are coal gasification and liquefaction processes. Products are the primary marketable fuel and feedstock materials such as low, medium, and high Btu gas; and solid and liquid hydrocarbons derived from coals. By-products are all other potentially usable components of coal conversion system yields.

PRODUCTS AND BY-PRODUCTS OF FUEL SYSTEMS

Figure 1 for coal gasification and Figure 2 for coal liquefaction define the major boundaries of products and by-products for these coal conversion systems. As indicated, basic process modules such as methanation, compression and dehydration, sulfur recovery, fractionation and hydrotreatment fall within the products and by-products area. Any other process and control techniques that might be applied for the recovery and upgrading of any product or by-product from such coal conversion systems would also be within the project's scope.

Coal Gasification

Table 1 shows coal gasification processes of current and potential interest along with their expected products and by-products. Principal subdivisions of coal gasification processes are in the low, intermediate, and high temperature operations. These may be further subdivided by operating pressure. Table 2 illustrates the quantities of products and by-products generated by a few selected processes.

A definite pattern emerges from examination of Table 1. The low temperature gasification processes tend to show a complete product and by-product slate, extending from fuel gas to ash or slag. As the temperature of gasification increases, recoverable quantities of

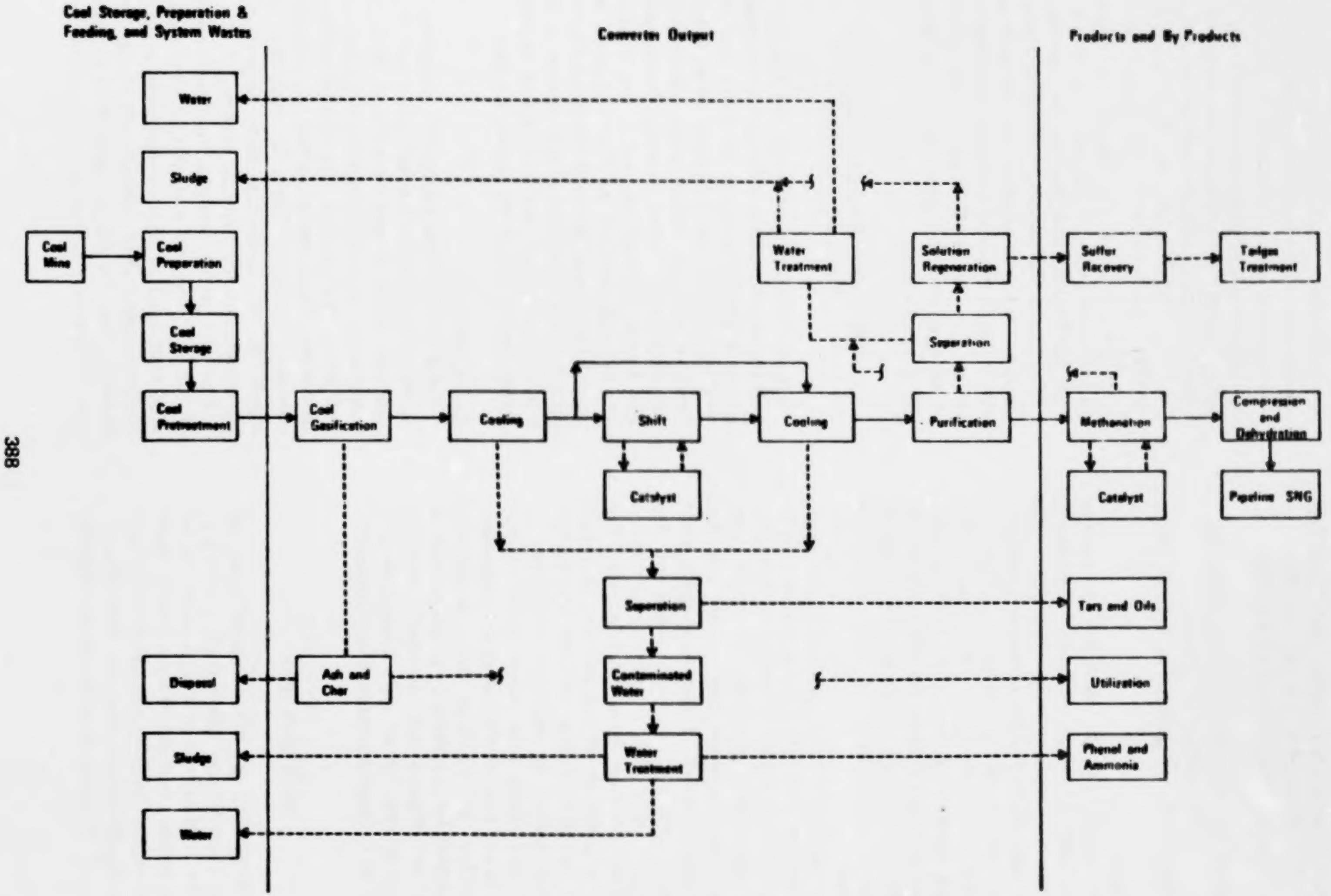
Coal Storage, Preparation & Feeding, and System Wastes
Converter Output
Products and By Products
Water
Sludge
Coal Mine
Coal Preparation
Coal Storage
Coal Pretreatment
Coal Gasification
Cooling
Shift
Catalyst
Cooling
Water Treatment
Separation
Solution Regeneration
Purification
Sulfur Recovery
Tailgas Treatment
Methanation
Catalyst
Compression and Dehydration
Pipeline SNG
Separation
Tars and Oils
Contaminated Water
Utilization
Water Treatment
Phenol and Ammonia
Ash and Char
Disposal
Sludge
Water

Figure 1. Hypothetical gasification flow diagram.

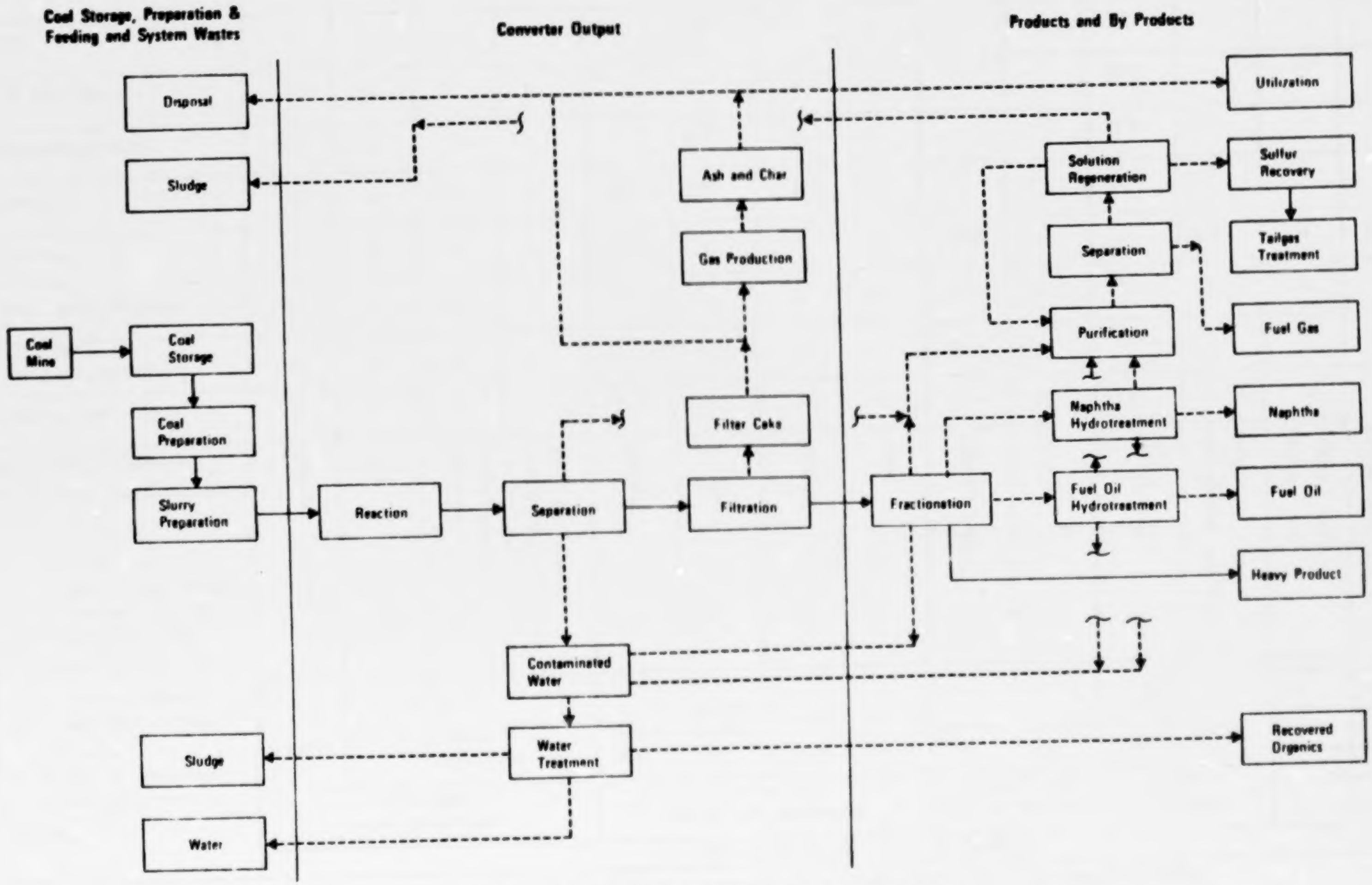
Coal Storage, Preparation & Feeding and System Wastes
Converter Output
Products and By Products
Disposal
Sludge
Coal Mine
Coal Storage
Coal Preparation
Slurry Preparation
Reaction
Separation
Contaminated Water
Water Treatment
Sludge
Water
Ash and Char
Gas Production
Filter Cake
Filtration
Fractionation
Solution Regeneration
Separation
Purification
Naphtha Hydrotreatment
Fuel Oil Hydrotreatment
Utilization
Sulfur Recovery
Tailgas Treatment
Fuel Gas
Naphtha
Fuel Oil
Heavy Product
Recovered Organics

Figure 2. Hypothetical liquefaction flow diagram.

TABLE 1

COAL GASIFICATION PROCESSES PRODUCT/BYPRODUCT AND FUEL SYSTEM SIMILARITIES

LEGEND:

P – Product/By-Product present in recoverable quantities.

Neg. – Negligible or small amounts present.

– Stream present in traces.

N.A. – Information not available, not complete, or not reported at this time.

	CLASSIFICATION OF FUEL SYSTEMS													
	Low Temperature Fixed Bed				Intermediate Temperature Fluidized Bed				High Temperature Entrained Bed		Dolomite Acceptor		Coal Pyrolysis	
	Low Pressure	Intermediate Pressure			Low Pressure	Inter-mediate Pressure	High Pressure		Low Pressure	High Pressure	Intermediate Temperature Intermediate Pressure		Entrained Inter. Temp. Low Pressure	Fluid Bed Inter. Temp. Inter. Pressure
Products/By–Products	Wellman – Galusha	Lurgi	BGC/Lurgi Slagging Gasifier	Pressurized Stirred Fixed Bed – Morgantown	Winkler	U – Gas	Synthane	Hygas	Koppers–Totzek	Bi–Gas	CO_2 Acceptor	Westinghouse–Advanced Gasifier	Battelle – Ash Agglomerating	Garretts Coal Gasification
High BTU Gas – SNG	P	P	P	–	P	–	P	P	P	P	P	–	P	P
Low (Intermediate) BTU Gas	P	P	P	P	P	P	–	–	P	–	–	P	P	P
H_2S – Acid Gas/Sulfur	P	P	P	P	P	P	P	P	P	P	P	P	P	P
Ammonia	P	P	P	P	N A	P	P	P	Neg.	P	P	N.A.	P	N.A.
Phenols	P	P	P	P	Neg.	Neg.	P	P	–	–	N.A.	–	–	–
Naphthas/Benzenes	N.A.	P	P	–	–	N.A.	P	P	–	–	N.A.	–	–	–
Tar Oils/Light Oils	P	P	P	P	–	Neg.	P	P	–	–	N.A.	–	–	–
Tars	–	P	P	P	–	Neg.	P	–	–	–	N.A.	–	–	P
Char/Unreacted Coal	P	–	–	P	P	P	P	P	–	–	P	–	–	P
Ash/Slag	–	P	P	P	–	–	–	–	P	P	–	P	P	–

TABLE 2

PRODUCTS/BYPRODUCTS OF DIFFERENT COAL GASIFICATION PROCESSES

Products/By-Products	Wellman-Gallusha	Lurgi	K-T	Bumines Stirred Bed	Winkler	Synthane	Hygas
Product Gas, SCFD	28.4MM (170 BTU/SCF)	288 MM (SNG)	524 MM (290 BTU/SCF)	995 MM (160 BTU/SCF)	912 MM (280 BTU/SCF)	250 MM (SNG)	260 MM (SNG)
Sulfur, lb/hr	777	15,600	23,600	24,200	50,400	11,400	55,500
Tars, lb/hr	1,153	88,800	neg.	75,600		43,200	
Tar Oil, lb/hr		48,600	neg.				
Phenol, lb/hr	120	11,300	neg.		neg.	4,000	1,300
Ammonia, lb/hr (anhydrous)	219	21,400	neg.	11,100	to claus	13,200	11,300
Hydrocarbon, lb/hr		20,000 (naphtha)				7,400 (BTX,naphta)	39,800
Char/Ash, lb/hr (Slag)	1,768 (ash)	476,000 (ash)	24,400 (ash,slag)	114,100 (ash)	372,500 (char)	362,000 (char)	139,000 (char)
Coal, lb/hr Feed	21,000 Bitum. 3.9% S	1.94 MM 1.07% S	0.7MM 3.8% S	0.7MM W. Ky.#9 3.9% S	1.68 MM Lignite 3.3% S	1.18 MM Pitts.Seam 1.6% S	1.06 MM Ill.#6 4.75% S

heavier tars begin to disappear in favor of lighter products. For the high temperature gasification processes, essentially the only product is fuel gas or products for synthesis; other by-product quantities are too low for recovery to be economic.

Operating pressure also changes yields, as shown in Table 1. As the pressure increases, the product slate becomes heavier. For example, in intermediate temperature processes, products such as naphthas, tar oils, and tars proceed from zero or negligible quantities to significant quantities as operating pressure increases.

For some reason naphtha doesn't appear in the reported products from the Stirred Fixed Bed Process and the Wellman-Galusha process[1,2,3,4,7,8]. From analogy with the other low temperature and intermediate temperature processes, a naphtha cut would be anticipated from both these systems. It is surmised that either the data available are incomplete, or perhaps the yields as reported include the naptha fraction as part of the tar oil stream. The pattern shown in this table indicates that the product slate for other coal gasification processes could be predicted by comparing the gasifier operating conditions with those listed.

Coal Liquefaction

Table 3 shows the relationship between various coal liquefaction processes and the product slates from these processes. In this table distinct patterns of product slates do not readily emerge as in the coal gasification processes. However, the following observations can be made.

- All the liquefaction processes produce an acid gas stream which will contain sulfur and other contaminants. In this regard, they are similar to coal gasification processes, which also produce an acid gas stream. Consequently, H_2S removal and sulfur recovery will be required for all coal processing plants.
- The liquid product distribution shows a range from syncrudes to naphtha and gas oils. However, all will contain varying amounts of sulfur, nitrogen, and metal contaminants which will have to be removed by subsequent upgrading treatments.
- Only the solvent refined coal (SRC) process yields a solid fuel. In all other processes, additional hydrogenation results in the formation of liquid products.
- Almost all the processes produce a char (coke and unreacted coal combined with ash) by-product with some fuel value. These by-products will require additional processing (e.g., specifically-designed combustion units) to utilize the carbon value and, thereby, increase the energy efficiency of the conversion process.
- Phenols and/or ammonia will be present in the aqueous waste streams in most cases and could be recovered as by-products.

Of all the liquefaction processes, solvent refined coal is the most developed. Two SRC pilot systems, 6 and 50 tons/day, are currently operating with various coals. Based on these results, salable product and by-product distribution for a nominal 20,000 ton/day plant using a Kentucky coal, containing 3.45 percent sulfur and 10.4 percent ash on dry basis, was calculated as follows:

Product	**Quantity, Ton/day (*)**
SRC	9,950
Light Oils (IBP-350° F)	750
Medium Oils (350-450° F)	2,210
Heavy Oils (450-780° F)	166
Fuel Gas	361
Sulfur	450
Ammonia (25%)	37
Phenolics	28

(*) Based on input coal (2% moisture) of 21,011 ton/day.

Effect of Coal Type

While the type of coal charged will not significantly affect the kinds of products and by-products generated by conversion, it will significantly affect how their quantities are distributed. For a particular process, coals with higher sulfur and nitrogen concentrations would obviously give higher proportions of S and NH_3 by-products. More information and testing with different coals will be necessary to establish the effects of coal type on the

TABLE 3

COAL LIQUEFACTION PROCESSES—PRODUCT/BYPRODUCT AND FUEL SYSTEM SIMILARITIES

LEGEND:

P – Product/By-Product present in recoverable quantities.

Neg.– Negligible or small amounts present.

– Stream present in traces.

N.A. – Information not available, not complete, or not reported at this time.

CLASSIFICATION OF FUEL SYSTEMS

Products/By -Products	Catalytic Hydrogenation			Solvent Extraction		Hydrocarbonization		Pyrolysis	
				Non-Catalytic Solvent Hydrogenation	Catalytic Solvent Hydrogenation	Intermediate Temperature	High Temperature	Low Temperature Fluid Bed	Intermediate Temperature Entrained Bed
	H–Coal	Synthoil	Gulf Catalytic Coal Liquefaction	Solvent Refined Coal (SRC)	EXXON Donor Solvent Process	Coalcon Hydrocarbonization	Clean Coke Multi-Product Process	Char, Oil Energy Development (COED)	Garrett Process
High B.T.U. Gas – SNG, LPG, ethylene, hydrocarbon, product gas.	P	P	N.A.	P	P	P	P	–	P
Low (Intermediate) BTU Gas – Fuel Gas, Synthesis Gas	–	–	N.A.	–	–	–	–	P	P
H_2S Acid Gas/Sulfur	P	P	P	P	P	P	P	P	P
Ammonia	P	P	P	P	N.A.	P	P	N.A.	N.A.
Phenols	Neg.	N.A.	P	P	N.A.	P	P	P	–
Benzenes	N.A.	N.A.	P	–	N.A.	P	P	P	–
Naphtha, Gasoline	P	–	P	P	P	P	P	–	–
Syncrudes	P	P	P	–	–	–	–	P	P
Middle Distillates, Fuel Oil	P	–	P	P	P	P	–	–	P
Gas Oils, Neutral Oils, Chemical Oils	P	–	P	–	P	P	P	–	–
Residual Fuel Oils	P	P	P	P	–	–	–	–	–
Tars (Tar Acids and Tar Bases)	–	–	–	–	–	P	P	–	P
Solvent Refined Coal	–	–	–	P	–	–	–	–	–
Char/Coke/Unreacted Coal	P	P	N.A.	P	–	P	P	P	P
Ash/Slag	P	–	N.A.	P	P	–	P	–	–

distribution of products and by-products for each coal conversion process.

POLLUTION CONTROL NEEDS

A variety of chemical compounds are generated in the form of products, by-products,and wastes during coal gasification andliquefaction processing. Many are toxic pollutants. For example,

- Sulfur compounds such as H_2S, SO_2, mercaptans, COS
- Nitrogen compounds such as NH_3, HCN, NO_x
- Hydrocarbons, polynuclear aromatics, heterocyclic compounds.

The objective of control technology development is to permit the fullest utilization of the different products and by-products while controlling environmental pollution within acceptable levels.

Products and By-products

As Fuel. The purpose of coal conversion systems is to produce fuels and chemical feedstocks. Combustion gases from the fuel products should preferably be capable of direct discharge to the atmosphere with no further treatment. This will generally require prior removal of sulfur compounds and particulates in the coal conversion process. In addition, nitrogen compounds will also have to be removed tobring NO_x emissions after combustion within acceptable limits.

For example, high temperature H_2S cleanup processes for the purification of low and medium Btu gas will increase the overall energy efficiency of the coal conversion process, but will create NO_x emission problems. The nitrogen compounds (e.g. ammonia) in the raw gas are not removed by these cleanup processes, so if the "purified" fuel gas is charged directly to a furnace, the nitrogen compounds will be converted to NO_x and exit in the flue gas. This calls for development of control technology that can be used in conjunction with high temperature gas purification processes for removing the nitrogen compounds prior to combustion.

A number of by-product streams may also serve as fuel. These include tail gas streams, tarry and oily liquids and chars. Control techniques will be required for sulfur, particulates, and NO_x emissions in these cases also.

As Chemical Feedstocks. Almost all products and by-products from coal conversion units may be used as chemical or petrochemical plant feedstocks. For example, low and medium Btu gas from coal gasification may be used as the starting material for production of hydrogen, ammonia, methanol, or Fischer-Tropsch liquids. For all these processes, pretreatment of the feed to remove the sulfur contaminant is necessary.

The liquids from coal conversion plants can serve as feedstocks for production of benzene, toluene, and xylene as well as for higher aromatics such as naphthalene. In addition, specialty solvents with high aromatic content may be produced. The coal-derived liquids used for aromatic production may be charged either to catalytic reforming units or dealkylation units. Before catalytic reforming, the liquid must be pretreated to remove sulfur and nitrogen impurities. Dealkylation takes place simultaneously with gasification of contaminants. The gaseous contaminants must be removed by control techniques such as scrubbing.

Gaseous Wastes

Generally, gaseous emissions from coal conversion plants originate from the following sources: raw material handling and pretreatment; vent gases from startup, shutdown and lock hopper operations; by-product recovery, storage and upgrading; waste treatment; acid gas removal and sulfur recovery; catalyst regeneration; and power generation. Various sulfur, nitrogen, hydrocarbon compounds, and particulates are present in air emissions.

Air emissions are controlled by the following four basic control modules:

- Sulfur control
- Particulate control
- Hydrocarbon control
- Nitrogen oxide control

At present, sulfur is the only by-product recovered from gaseous emissions to any large extent.

Liquid Wastes

The liquid waste (gas liquor) contains tars, tar oils, phenols, and ammonia as well as virtually every contaminant found in the fuel conversion systems. Large amounts of particulates, CO_2, H_2S, chloride and sulfate are present. Cyanide and ferrocyanide occur in the aqueous layer. Reported trace elements include antimony, arsenic, boron, bromine, cadmium, fluorine, lead, mercury, and nickel.

Little information exists as to how these contaminants will be distributed throughout the recovered by-products. Many contaminants will probably appear in the crude by-products. These pollutants would have to be removed for environmental protection.

At least five different by-product streams are produced from typical Lurgi plant liquid wastes: tar, tar oil, crude phenol, ammonia, and sulfur. The foregoing by-products are recovered from a gas liquor with the following typical composition:

Component	**Approximate Composition, ppm**
Phenols	3,000-4,000
Ammonia (free)	500-750
Ammonia (fixed)	100-200
Sulfides (total)	200-250
Suspended tar, oil	5,000
Cyanides	50
CO_2	10,000
Fatty acids	500

The proposed El Paso Burnham complex Lurgi plant will produce 288 million SCFD synthetic pipeline quality gas, gasifying 1.07% sulfur coal at the rate of 1.944 million lb/hr. Figure 3 shows the distribution of the various by-products from this plant. A sizable portion of the by-products are absorbed in, or condense out with, the organic and aqueous condensates as the gases are first quenched with water and then cooled. The heavier tars separate out first in the gasifier waste heat boiler and are called "tarry gas liquor." Further downstream, in the gas cooling section, the tar oils with the remaining tars condense out forming the "oily gas liquor." In the acid gas removal step, H_2S and naptha separate out. Naphtha goes directly to a storage tank. H_2S-containing acid gases are processed further to recover the sulfur. Table 4 gives the material balance for the gas liquor treatment[5].

Ammonia and sulfur will be recovered as commercial-grade materials, but further upgrading will be required to meet demands for explosives and fertilizers. Other by-products will also require upgrading[6].

Solid Wastes

Solid wastes are composed of the ash residue plus the accompanying unrecovered carbon or hydrocarbons from the coal charge. If filtration is used in the liquefaction process for ash separation, filter precoat will also be present.

To make coal processing economic, the carbon values from char should be recovered. Two recovery possibilities are on-site combustion of char for steam generation or for hydrogen manufacture. When used in this manner, removal of particulates and sulfur will be required to clean up the stack gases before discharging to atmosphere.

Solid residues such as ash and filtercake will contain trace metals from coal. Recovery of some of these minerals may be possible in the future. If not, then the solid wastes must be disposed of in ways that protect the environment.

In considering pollution control needs, it is necessary to stay cognizant of the interrelationships existing among liquid, gaseous and solid wastes. For example, spent catalysts can present a solids disposal problem if not reused, or cause an air pollution problem when regenerated. The contaminants that normally deactivate catalysts are sulfur compounds, nitrogen compounds, and heavy metals. Catalyst activity can be maintained or lengthened by burning these contaminants off the catalysts. The off gases from catalyt regeneration will contain sulfur, nitrogen, and hydrocarbon compounds and will also require controls to meet air pollution emission requirements.

CONTROL TECHNOLOGY

This section reviews some of the important existing control technologies or classes of technologies.

Earlier discussion established that a full slate of products, extending from fuel gas to ash,

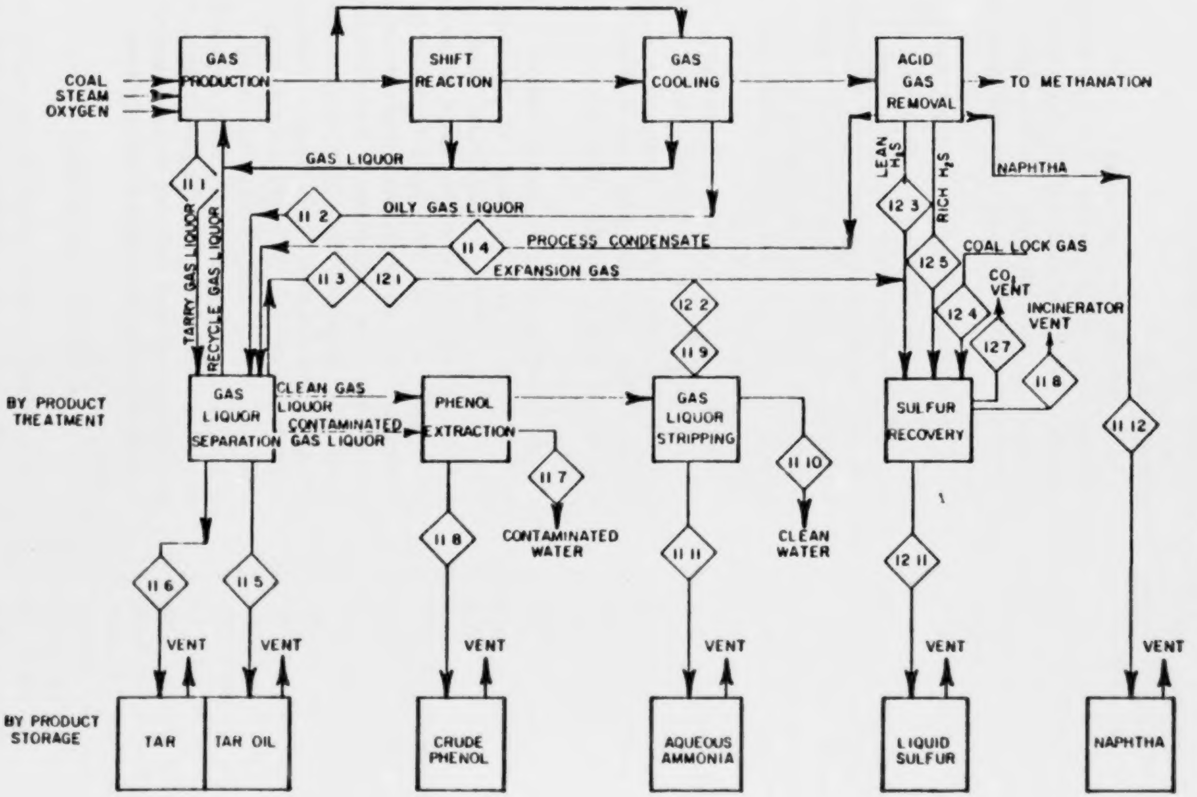
COAL
STEAM
OXYGEN
GAS PRODUCTION
SHIFT REACTION
GAS COOLING
ACID GAS REMOVAL
TO METHANATION
GAS LIQUOR
LEAN H2S
RICH H2S
NAPHTHA
11 1
TARRY GAS LIQUOR
RECYCLE GAS LIQUOR
11 2
OILY GAS LIQUOR
11 4
PROCESS CONDENSATE
11 3
12 1
EXPANSION GAS
12 3
12 5
COAL LOCK GAS
CO2 VENT
12 4
12 7
INCINERATOR VENT
11 8
12 2
11 9
BY PRODUCT TREATMENT
GAS LIQUOR SEPARATION
CLEAN GAS LIQUOR
CONTAMINATED GAS LIQUOR
PHENOL EXTRACTION
GAS LIQUOR STRIPPING
SULFUR RECOVERY
11 12
11 7
CONTAMINATED WATER
11 10
CLEAN WATER
11 6
11 5
11 8
11 11
12 11
VENT
VENT
VENT
VENT
VENT
VENT
BY PRODUCT STORAGE
TAR
TAR OIL
CRUDE PHENOL
AQUEOUS AMMONIA
LIQUID SULFUR
NAPHTHA

Figure 3. By-product from Lurgi plant.

TABLE 4

MATERIAL BALANCE FOR GAS LIQUOR TREATMENT

Stream Number	11.1	11.2	11.3	11.4	11.5	11.6	11.7	11.8	11.9	11.10	11.11	11.12
Stream Description	Terry Gas Liquor	Oily Gas Liquor	Expansion Gas	Process Condensate	Tar Oil	Tar	Contaminated Gas Liquor	Crude Phenol	Acid Gas	Clean Water	Aqueous Ammonia	Naptha
Gas Phase, lb/hr												
Component												
Water	--	--	2,030	--	--	--	--	--	8,870	--	--	--
Tar	--	--	--	--	--	--	--	--	--	--	--	--
Tar Oil	--	--	--	--	--	--	--	--	--	--	--	--
Recoverable Crude Phenol	--	--	--	--	--	--	--	--	--	--	--	--
Unrecoverable Phenol & Organic	--	--	--	--	--	--	--	--	--	--	--	--
Ammonia	--	--	--	--	--	--	--	--	--	--	--	--
H_2S	--	--	315	--	--	--	--	--	280	--	--	--
CO_2	--	--	59,700	--	--	--	--	--	8,570	--	--	--
CO	--	--	70	--	--	--	--	--	--	--	--	--
CH_4	--	--	50	--	--	--	--	--	--	--	--	--
Monohydric Phenols	--	--	--	--	--	--	--	--	--	--	--	--
Polyhydric Phenols	--	--	--	--	--	--	--	--	--	--	--	--
Other Organics	--	--	--	--	--	--	--	--	--	--	--	--
Contained Sulfur	--	--	--	--	--	--	--	--	--	--	--	--
Naphtha	--	--	--	--	--	--	--	--	--	--	--	--
Total Dry Gas, lb/hr	--	--	62,165	--	--	--	--	--	17,720	--	--	--
Liquid Phase, lb/hr												
Component												
Water	165,000	1,180,000	--	103,000	--	--	164,000	--	--	1,190,000	82,000	--
Tar	79,900	8,900	--	--	--	88,800	--	--	--	--	--	--
Tar Oil	14,600	34,000	--	--	48,600	--	--	--	--	--	--	--
Recoverable Crude Phenol	210	11,100	--	--	--	--	--	--	--	--	--	--
Unrecoverable Phenol & Organic	130	4,100	--	--	--	--	--	--	--	--	--	--
Ammonia	--	21,600	--	--	--	--	--	--	--	240	21,400	--
H_2S	300	300	--	--	--	--	--	--	--	--	10	--
CO_2	17,200	54,800	--	--	--	--	--	--	--	--	3,660	--
CO	70	--	--	--	--	--	--	--	--	--	--	--
CH_4	40	--	--	--	--	--	--	--	--	--	--	--
Monohydric Phenols	--	--	--	--	--	--	3	9,100	--	24	--	--
Polyhydric Phenols	--	--	--	--	--	--	70	1,600	--	900	--	--
Other Organics	--	--	--	--	--	--	60	560	--	3,200	--	--
Contained Sulfur	--	--	--	--	(73)	(240)	--	--	--	--	--	--
Naphtha	--	--	--	--	--	--	--	--	--	--	--	20,000
Total Liquid, lb/hr	277,450	1,314,800	--	103,000	48,600	88,800	164,133	11,260	--	1,194,364	107,070	20,000

NOTE: Crude estimate based on following assumptions:

1. Monohydric phenols reduced to 20 PPM per Lurgi
2. 60% of polyhydric phenols recovered
3. 15% of other organics recovered
4. Crude phenol stream contains 5% other organics
5. Phenols recovered are 50% monohydric and 50% polyhydric

- Assumptions 2-4 were presented by Beychok in reference (1) for a crude determination of gasification effluent composition.

can be obtained from either the gasification or liquefaction process. Furthermore, the impurities in these streams are generally similar, including sulfur and nitrogen compounds, heavy metals, and particulates.

Identical products from coal gasification and coal liquefaction processes will contain the same contaminants and therefore, may be processed in similar type pollution control systems. For example, sulfur contamination of fuel gas or phenol contamination of aqueous wastewater, whether from coal gasification or coal liquefaction, could have similar treatment and recovery units.

It makes sense then to discuss control technologies primarily in terms of the class of contaminants. Product/by-product identification can serve as a secondary variable while coal gasification or liquefaction is of incidental importance. Control technologies discussed here will be limited to the following classes of contaminants:

- Sulfur and nitrogen compounds
- Particulates
- Heavy metals/trace contaminants

Other pertinent control technologies are touched on briefly, but many such as for hydrocarbon, phenol removal, and wastewater treatment, cannot be covered in depth at this time.

Sulfur and Nitrogen Compounds

Combined sulfur and nitrogen in the products and by-products from coal conversion plants can be converted to H_2S and NH_3 by hydrogenation, or to SO_2 and NO_x by oxidation.

H_2S can be scrubbed from the gaseous products and converted to elemental sulfur. Similarly, SO_2 can be removed from the gases, either by dry or wet scrubbing. The scrubbed SO_2 may then be converted to a variety of different forms, such as elemental sulfur, sulfates, or bisulfites, for disposal or utilization. Control of NO_x compounds by similar scrubbing processes are in the state of development. Currently, various combustion modifications are the best means to control NO_x.

Hydrogenation. In the presence of hydrogen, hydrogenation of the sulfur and nitrogen can occur either thermally (as in coal gasification plants) or catalytically (as in catalytic coal liquefaction plants). For example, the gasification of residue and chars to produce hydrogen results in the formation of H_2S and NH_3.

Catalytic hydrotreating is a well established process in the petroleum industry for the removal of sulfur and nitrogen contaminants. It has been found in the petroleum industry that the operating conditions required for denitrification are much more severe than those required for desulfurization, especially if organic nitrogen is present in thermally cracked stocks. Also, special design care is required for treating some light distillates (as from ethylene plants) because of the gum-forming tendencies of these stocks.

Distillates derived from ethylene plants appear to be the most analogous to those from coal for catalytic hydrogenation treatments. The process flow module should be similar, with hydrotreating followed by fractionation or stripping to remove the H_2S, NH_3, and H_2O formed in the reactors. Prevention of equipment plugging from gum formation is an important design consideration in both cases.

When heavey distillates are hydrotreated in fixed bed reactors, the process module is similar to that for catalytic treating of light distillates--hydrotreating followed by fractionation or stripping. However, the hydrotreating conditions of temperature, total pressure, hydrogen partial pressure, and space rate are more severe than those used for light distillates. At these more severe conditions, and with higher concentrations of sulfur and hydrogen in the process streams, high alloy materials of construction are required. Desulfurization achieved in these units is in the range of 75 to 90%.

The problem with the use of fixed beds for hydrotreating heavy distillates is rapid deactivation of the catalyst caused by heavy metals build-up. Thus, some means of maintaining the catalyst activity by total or partial replacement of the catalyst is necessary. Other reactor designs, such as fluidized or ebullating beds, may circumvent this difficulty. With these designs spent catalyst can be continuously removed from the reactor and replaced by fresh catalyst. Regardless of reactor design, the general overall processing module of hydrotreating followed by stripping would be the same.

Hydrotreating of coal-derived heavy distillates would be expected to follow the same process modules as for petroleum-derived heavy distillates. The concentration of heavy metals in the distillate cut would dictate the type of reactor design necessary. Heavy distillate from both coal gasification and coal liquefaction plants would require hydrotreating units having similar modules.

The catalysts used for hydrotreating are of the cobalt-molybdenum type which resist catalyst poisoning. Catalyst deactivation results from buildup of carbonaceous deposits or heavy metals. Carbonaceous matter can be readily removed from the catalyst in-situ, by steam-air oxidation. Heavy metals cannot be removed. But in the case of light distillates, they are not present in significant concentrations, and should not present a contamination problem. Additionally, catalyst will become deactivated over a long period by loss of active surface area due to time-temperature effects.

H_2S Removal and Sulfur Recovery. A number of commercial processes are available for removing sulfur from fuel gas, as shown in Table 5. These operate at low temperature, so if the scrubbing unit is followed by methanation, the scrubbed gas must be reheated.

To avoid reheating, and thereby increase the energy efficiency of the process, new high temperature H_2S cleanup units are under development (Table 6). One disadvantage of high-temperature cleanup schemes is omission of the initial quench step, which removes NH_3 and particulates from the raw gas. So, removal of the ammonia from fuel gas at high temperature requires further development. High temperature removal of the particulates may be affected by one of the processes shown in Table 7.

Numerous sulfur recovery processes of the direct conversion type exist. These can be classified as either dry oxidation or liquid phase oxidation. The principle of operation involves the oxidation of sulfur compounds to elemental sulfur. The two most widely used direct conversion processes are the Claus (dry oxidation) and the Stretford (liquid phase oxidation) processes.

The commercial Stretford process recovers inorganic sulfur from acid gases containing less than 15% H_2S. A packed absorber removes H_2S from acid gases, using Stretford solution absorbent, which is mainly sodium metavanadate, sodium anthraquinone disulfonate (ADA), sodium carbonate, and bicarbonate in water. Sulfur recovery between 98%-99% is possible. This process is insensitive to H_2S/CO_2 ratio, and operates over wide pressure ranges. Temperature limitations are between ambient to 120° F.

The process does not remove organic sulfur, and it requires pretreatment removal of large quantities of SO_2, HCN or heavy hydrocarbons. It produces a purge wastewater stream containing spent Stretford solution, which will require treatment[9].

The Claus process effectively controls sulfur emissions and recovers elemental sulfur from gas streams containing high concentrations of H_2S (at least 10-15%). In most cases, tail gas treatment is also necessary.

Tail Gas Treatment. Tail gas cleanup processes, when combined with a Claus unit, can provide an overall sulfur removal efficiency of up to 99.9%. Commercially available tail gas cleanup processes include:

Process Name	**Type**
SCOT	Catalytic hydrogenation of sulfur compounds to H_2S and then removal by absorption processes or recycle to a Claus unit.
Beavon	
Cleanair	
Cataban	
Trencor-M	
Sulfreen	Continuation of Claus reaction at low temperatures (245-270° F)
CBA	

An alternative to tail gas treatment is to incinerate the gases and then scrub the resulting SO_2. This set of processes was developed to handle tail gases from furnaces, smelters, and pulp mills, where SO_2 is the main pollutant rather than H_2S.

SO_2 scrubbing systems have several advantages over the H_2S processes. The scrubbers are less affected by process upsets, are not susceptable to catalyst poisons, and can scrub SO_2 from very dilute mixtures. But scrubbing

TABLE 5

LOW TEMPERATURE H_2S CLEANUP PROCESSES

PROCESSES	ABSORBENT	STATUS
Chemical Solvent Type		
MEA	Monoethanolamine	Commercial
DEA	Diethanolamine	Commercial
TEA	Triethanolamine	Commercial
Alkazid	Potassium dimethyl amino acetate	Commercial
Benfield	Activated potassium carbonate solution	Commercial
Catacarb	Activated potassium carbonate solution	Commercial
Physical Solvent Type		
Sulfinol	Sulfolane + di-isopropanolamine	Commercial
Selexol	Polyethylene glycol ether	Commercial
Rectisol	Methanol	Commercial
Direct Conversion		
Stretford	Na_2CO_3 + anthraquinone sulfonic acid	Commercial
Townsend	Triethylene glycol	Commercial
Drybed Type		
Iron Sponge	Hydrated Fe_2O_3	Commercial

TABLE 6

HIGH TEMPERATURE H_2S CLEANUP PROCESSES

PROCESS	ABSORBENT	STATUS
Bureau of Mines	Sintered pellets of Fe_2O_3 (25%) and fly ash	Pilot
Babcock and Wilcox	Fe_2O_3	Experimental
CONOCO	Half calcined dolomite	Pilot
Air Products	Calcined dolomite	Abandoned
Battelle Northwest	Molten carbonates (15% $CaCO_3$)	Pilot
IGT-Meissner	Molten metal (proprietary)	Conceptual
Air Products	Fe_2O_3	Experimental

TABLE 7

HIGH TEMPERATURE PARTICULATE REMOVAL SYSTEMS

TYPE OF REMOVAL SYSTEM	MANUFACTURER	STATUS
Mechanical Collectors		
Cyclones	Buell, Ducon & Others	Commercial
Tornado	Aerodyne	Commercial
Bed Filters		
Granular	Combustion Power Co.	Under Development
	Ducon	Under Development
Panel	C.U.N.Y.	Under Development
Rex	Rexnord	Commercial
Sonic Agglomeration Collection Systems		
Alternating Velocity Precipitator	Braxton	Under Development
Scrubbers		
Fused salts	Battelle	Under Development
Filters		
Metal and Ceramic	Selas and Others	Commercial
Electrostatic Precipitators	Research-Cottrell and others	Commercial

processes are more expensive than other tail gas treatment methods.

Ammonia Recovery. NH_3 formed by the hydrogenation reactions can be scrubbed from the reaction gases by water and subsequently recovered by steam stripping. Several processes are available, for example--Chevron,Phosam-W, and others based on lime treatment to free fixed ammonia for later steam stripping.

Phosam-W, a U.S. Steel Corp. developed process, uses aqueous acid ammonium phosphate solution to scrub ammonia from gases. The scrubbed sour water is then stripped of ammonia with steam and the acid ammonium phosphate solution is recycled.

The Chevron process separates ammonia, carbon dioxide, and hydrogen sulfide from liquid waste streams. Another system, consisting of a pairing of Phosam-W and Firma Carl Still, recovers hydrogen sulfide (for sulfuric acid manufacture) and ammonia from sour water[10].

Particulates

Equipment for controlling particulates in gas streams includes cyclones, bag filters, electrostatic precipitators, and wet scrubbers. Particle size distribution is one of the important parameters necessary to predict the separation efficiency of these devices. High temperature removal of particulates may be effected by one of the processes shown in Table 7.

Heavy Metals/ Trace Contaminants

Heavy metals and trace contaminants are so numerous, and cover such a wide field of physical and chemical properties, that any discussion of control methods should be on an individual basis. Therefore, this paper offers only a few generalized remarks on this class of contaminants.

Determination of the concentration and distribution of heavy metals in the coal feed and in the effluents and product streams of the coal conversion plant is of prime importance. Some preliminary estimate of these values can be attempted by consideration of the physical and chemical characteristics of these elements, and of the compounds they may form in the system. However, ultimate testing and analysis in plant studies will be necessary to establish these distributions. These may then be compared to the allowable safe concentration limits, as set by EPA.

Another concern with regard to heavy metals is their effect on catalyst activity. Heavy metals contained in the feed to catalytic units often will be adsorbed on the surface of the catalyst, causing its deactivation. If, in a particular situation, this occurs at a very slow rate, the catalyst is merely discarded when its activity has fallen to an uneconomic level. In other cases, the catalyst may be protected by placing guard cases ahead of it, or by periodically or continuously drawing off some spent catalyst and replacing it with fresh catalyst. It should be noted here that spent catalyst may have high concentrations of heavy metals or other contaminants, and if regeneration is attempted, these contaminants could be released in a short period of time at high concentrations, causing a health problem.

Additional Control Technologies

A large number of other control technology techniques not covered here are applicable in upgrading operations of products and by-products. Examples include methanation, catalytic synthesis, catalytic cracking, hydrocracking, catalytic reforming, and fractionation. The other broad control areas are the gas, liquid, and solid waste treatment techniques. These and other control approaches are shown in Table 8[11].

CONTROL TECHNOLOGY ASSESSMENT AND DATA ACQUISITION

Little operating data on control technology for either pilot or commercial scale coal conversion systems exist in the literature. Data acquisition by actual field testing, therefore, should be given top priority for control technology.

In this regard, EPA has initiated projects to (1) design laboratory units needed to evaluate feasible controls for coal conversion products and by-products streams, and (2) develop laboratory treatability screening procedures to

TABLE 8

CONTROL APPROACHES

o Gas Treatment

- Mechanical Collection
- Electrostatic Precipitators
- Filters (fabric, granular, etc.)
- Liquid Scrubbers/Contactors (aqueous, inorganic, organic)
- Condensers
- Solid Sorbents (mol sieves, activated carbon)
- Incineration (direct and catalytic)

o Liquids Treatment

- Settling, Sedimentation
- Precipitation, Flocculation, Sedimentation
- Evaporation and Concentration
- Distillation, Flashing
- Liquid-Liquid Extraction
- Gas-Liquid Stripping
- Neutralization
- Biological Oxidation
- Wet Thermal Oxidation
- Activated Carbon Adsorption
- Ion Exchange System
- Cooling Tower (wet & dry)
- Chemical Reaction and Separation
- Centrifugation and Filtration

o Solids Treatment

- Fixation
- Recovery/Utilization
- Processing/Combustion
- Chemical Reaction and Separation
- Oxidation/Digestion
- Physical Separation (specific gravity, magnetic, etc.)

o Final Disposal

- Pond Lining
- Deep Well Reinjection
- Burial and Landfill
- Sealed-Contained Storage
- Dilution
- Dispersion

o Process Modification

- Feedstock Change
- Stream Recycle

o Combustion Modification

- Flue Gas Recycle
- Water Injection
- Staged Combustion
- Low Excess Air Firing
- Optimum Burner/Furnace Design
- Alternate Fuels/Processes

o Fuel Cleaning

- Physical Separation (specific gravity, surface properties, magnetic)
- Chemical Refining
- Carbonization/Pyrolysis
- Liquefaction/Hydrotreating (HDS, HDN, Demetallization)
- Gasification/Separation

o Fugitive Emissions Control

- Surface Coatings/Covers
- Vegetation
- Leak Prevention

o Accidental Release Technology

- Containment Storage
- Flares
- Spill Cleanup Techniques

TABLE 9

R & D ACTIVITIES TO UPGRADE COAL CONVERSION PRODUCTS/BYPRODUCTS

Investigator	Project Title	Funding
Arco Chemical Co.	Catalytic Hydrotreating of Coal-Derived Liquids	ERDA (Project Completed)
Bartlesvile Energy Research Center	Refining Process Technology	ERDA
The Dow Chemical Co. and Pittsburgh Energy Research Center	Chemicals from Coal Liquids	ERDA
Exxon Research and Engineering Co.	Chemical Properties of Synthoil Products and Feed	ERDA Exxon
Hydrocarbon Research, Inc.	Demetallization of Heavy Residual Fuel Oils	EPA
M.I.T.	Catalytic Desulfurization and Denitrification	EPA
Pittsburgh Energy Research Center	Petrochemicals from Synthesis Gas	ERDA
Sandia Labs	Mechanisms of Deactivation and Reactivation of Catalysts	ERDA
Universal Oil Products, Inc.	Characteristics of Coal-Derived Liquids	ERDA
Air Products	Characteristics of SRC Liquids	ERDA

TABLE 10

LIST OF PRODUCTS/BYPRODUCTS AND SOME OF THEIR FINAL PRODUCT POSSIBILITIES

Products/By-Products	Examples of Final Product Possibilities
1. Aqueous wastewater containing ammonia, phenol and tar, etc.	Ammonia, crude phenol and tar
2. Crude phenol	Natural phenol, refined cresylics, phenolic pitch
3. Tar and tar oil	Benzene, toluene and xylene (BTX)
4. Naphthas	Ethylene
5. H_2S Acid Gas/Sulfur	Sulfur/Sulfuric Acid
6. Spent Catalyst	Regenerated catalyst
7. Char	Hydrogen, or fuel gas
8. Ash	Recovered heavy metals
9. Low BTU gas, medium BTU gas	SNG, fuel, feedstocks for chemicals such as NH_3 and CH_3OH
10. High BTU gas	SNG, chemical feedstock
11. Syncrudes	Refinery products such as gasoline and fuel oil
12. Middle distillate oil	Fuel oil
13. Gas oils	Lubricants, cat-cracker feedstock
14. Residual fuel oils	Coke, fuel oil
15. SRC	Coal fuel, high purity coke

determine how an environmentally harmful stream can be made less harmful through application of appropriate control techniques.

Most of the control technologies discussed earlier are being used in the petroleum, petrochemical, and coke oven by-products industries. It is of utmost interest to know how these technologies are working, and whether their performance characteristics can be duplicated in the synthetic fuels industry.

For this reason, EPA is currently sponsoring a study of the coke oven by-products industry control techniques to determine which are applicable to the coal conversion industry. This work was begun recently and will be reported later. A companion study is being conducted to determine which of the control techniques from the petroleum industry are applicable to coal conversion systems.

A number of research and development activities are being funded by EPA and ERDA to upgrade coal conversion products and by-products. Some of these are shown in Table 9. The impetus for engaging in these activities is illustrated in Table 10 which presents examples of the many marketable chemicals potentially recoverable from the upgrading of coal conversion products and by-products.

CONCLUSIONS

The economic justification of coal conversion systems depends to a large extent on being able to develop technology (1) that will permit upgrading products and by-products into additional marketable chemicals and (2) that will accomplish this goal without substantive adverse impact on the environment.

Generally, product and by-product utilization will require removal of sulfur and nitrogen contaminants before their use as fuel or chemical feedstocks. Some of the more important control needs include H_2S, SO_2, NO_x, hydrocarbon and particulate removal from gaseous effluents; removal of phenol, ammonia, sulfide, dissolved organics, heavy metals, and cyanides from aqueous waste streams; and prevention of solid waste leachate problems. When such pollutants are removed from waste streams and converted to usable products, downstream waste treatment problems and environmental impacts are automatically improved. By-product recovery and upgrading control technologies are, therefore, an important part of the overall environmental management program.

Little operating data on control technology for either pilot or commercial scale coal conversion systems exist in the literature. At the present, most of the control technologies that are applicable for the products and by-products of coal conversion systems are being used in the petroleum, hydrocarbon, and coke oven industries. However, their applicability and limitations have yet to be determined by actual use and field testing with different coal conversion systems.

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SPECIFIC ENVIRONMENTAL ASPECTS OF FISCHER-TROPSCH COAL CONVERSION TECHNOLOGY

by

B. I. Loran and J. B. O'Hara
The Ralph M. Parsons Company
Pasadena, California

Abstract

A preliminary design of a commercial-scale Fischer-Tropsch plant producing liquid hydrocarbons plus substitute natural gas by indirect coal liquefaction has been completed. The units and processes utilized are reviewed to highlight the progressive removal from the streams of compounds or materials capable of contributing to air and water pollution. All final effluents released to the environment are estimated to be in compliance with applicable or related Federal and State standards.

Methods of environmental control for the following specific areas are discussed:

- *Fate of trace elements present in coal.*
- *Formation and destruction of metal carbonyls.*
- *Cyanide formation, partitioning among effluent streams, and final decomposition.*
- *Formation of coal-tar carcinogens and biohazards involved.*

There still exist some environmental aspects specific to coal conversion for which additional experimental data are required. Research and development programs that can provide this additional information are defined.

INTRODUCTION

Development of viable coal conversion technology is a national priority. A prime responsibility for development of this technology rests with the Energy Research and Development Administration—Fossil Energy (ERDA-FE). The Ralph M. Parsons Company is assisting ERDA-FE in reaching this objective by developing preliminary designs and economic evaluations for commercial coal conversion facilities. Preliminary commercial designs for four of these facilities have been completed so far, namely for a Demonstration Plant producing clean boiler fuels from coal, for a complex producing oil and power by COED (Coal Oil Energy Development) based pyrolysis coal conversion, for an Oil/Gas Plant using integrated coal conversion technology, and for a Fischer-Tropsch facility producing liquid hydrocarbons plus substitute natural gas by indirect coal liquefaction.

The definition of facilities and procedures to assure that environmentally acceptable plants can be designed and operated is integral to the design effort. The basis for establishing environmental control facilities and operating procedures is the many coal conversion process development units and pilot plants being operated in the United States plus experience gained from related industries such as petroleum processing.

This paper concerns specific environmental aspects of a Fischer-Tropsch facility. The technology involved, outlined in Figure 1, consists of coal gasification to produce a carbon dioxide/carbon monoxide/hydrogen syngas, purification of this gas to remove carbon dioxide and hydrogen sulfide, adjustment of composition to increase the hydrogen content, and catalytic conversion of the gas to form principally hydrocarbon liquids. Part of the unreacted syngas is upgraded by methanation to substitute natural gas (SNG). A version of this technology is presently applied on a commercial scale in the Republic of South Africa.

The Parsons conceptual commercial design incorporates advanced technology such as a high temperature-high pressure gasifier based on Bi-Gas principles and a flame-sprayed catalytic reactor for Fischer-Tropsch conversion. Both of these are in the development stage and require further work prior to the design and construction of commercial plants. Successful application of these technologies could lead to conversion of coal to liquid and gaseous fuels with an overall thermal efficiency of 70 percent. A report describing the conceptual design and economic analysis of the facility has been published.[1]

As conceived, the plant will be located adjacent to a coal mine in the Eastern Region of the

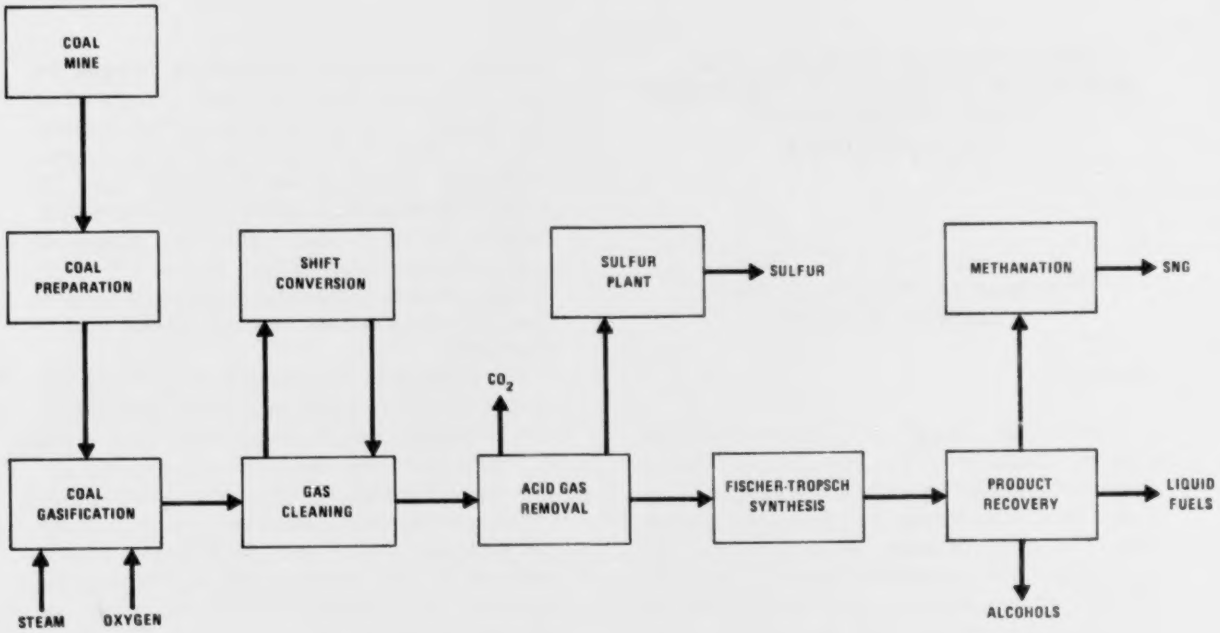
COAL MINE
COAL PREPARATION
COAL GASIFICATION
STEAM
OXYGEN
SHIFT CONVERSION
GAS CLEANING
CO_2
ACID GAS REMOVAL
SULFUR PLANT
SULFUR
FISCHER-TROPSCH SYNTHESIS
METHANATION
SNG
PRODUCT RECOVERY
LIQUID FUELS
ALCOHOLS

Figure 1. Simplified block flow diagram, Fischer-Tropsch conceptual plant.

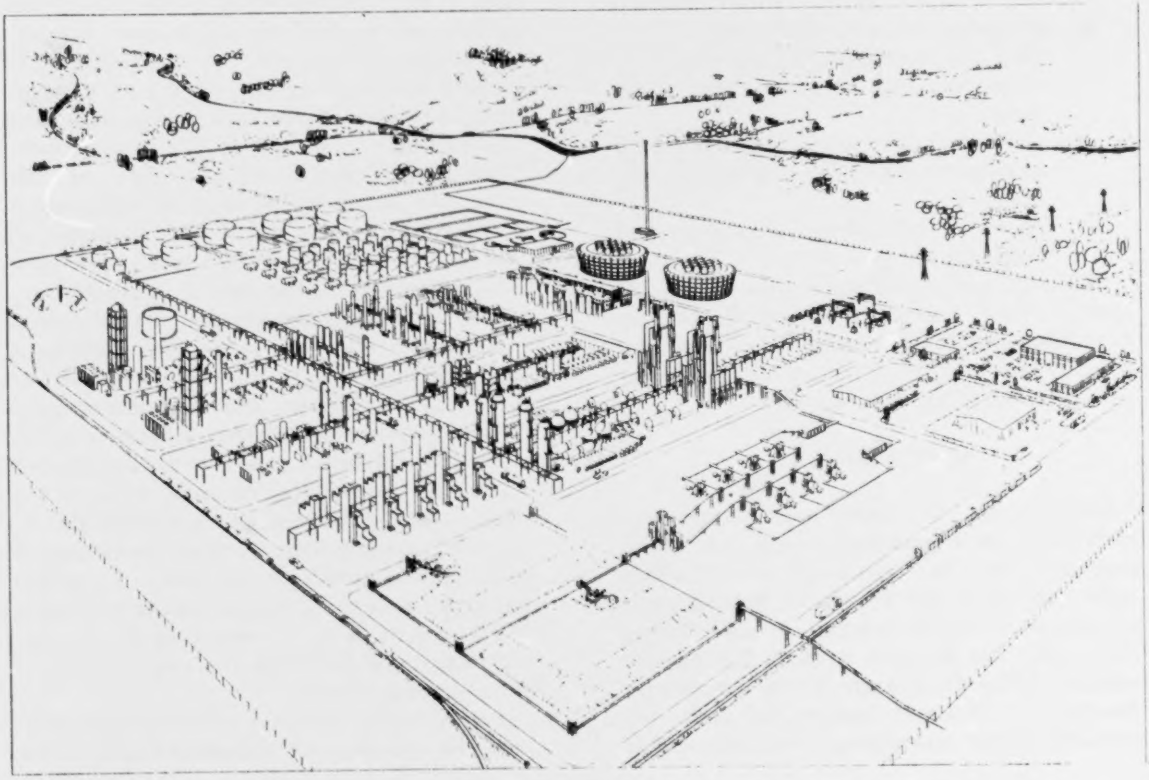

Figure 2. Artist's concept, Fischer-Tropsch plant.

Interior (coal) Province of the United States. The design is based on use of 27,000 metric tons per day (MgPD) [corresponding to 30,000 U.S. tons per day (TPD)] of cleaned bituminous coal, containing 1.1 percent nitrogen and 3.4 percent sulfur. The premium products obtained, containing nil sulfur or nitrogen, consist of 2,200 MgPD (2,400 TPD) naphthas, 1,900 MgPD (2,100 TPD) of diesel fuel, 650 MgPD (700 TPD) of fuel oil, and 6,000 MgPD (6,600 TPD) of SNG. Heat recovery provides all power and steam required to operate the complex; excess electric power for sale (140 megawatts) is also produced. An artist's concept of the Fischer-Tropsch complex is shown in Figure 2.

AIR POLLUTION ABATEMENT

The major air pollution abatement effort is aimed at desulfurizing the gases generated during the coal conversion process to make the fuels produced environmentally acceptable. In a Fischer-Tropsch plant, environmental and process goals coincide because the presence of sulfur inhibits the effectiveness of Fischer-Tropsch catalysts.

The air pollution abatement procedure is outlined in Figure 3, which shows the nature and amount of all streams vented to the air; these streams consist for the major part of inert gases (nitrogen and carbon dioxide). The effluent gases are shown vented separately to the air to identify the contribution of specific process units. In reality, however, all streams with the exception of the particulates from the coal drying plant are combined into a single stack before venting to the air.

The coal grinding and drying unit is the only source of particulate emissions. A baghouse system removes most of the particulates from the vent streams, with emissions to the air meeting both the Federal standard for thermal dryer gases and other standards related to coal gasification plants. The source of heat for the drying process is excess steam from the Fischer-Tropsch plant; no combustion gases are generated by the operation.

The coal gasifier receives powdered coal, steam, and oxygen and generates hydrogen, carbon monoxide, carbon dioxide, methane, hydrogen sulfide, and minor amounts of ammonia, carbon oxysulfide, cyanides, and sulfur dioxide. The reactor operates at high pressure (3.5 MPa, 500 psia) and temperatures (1650° C, 3000° F in the lower stage and 930° C, 1700° F in the upper stage). At these elevated temperatures, nil oils or tars are produced.

The gaseous stream carries all the char and ash produced on gasification of the coal; the largest part of these materials is removed by a series of cyclones, followed by a hot electrostatic precipitator. Recovered char is returned to the lower section of the gasifier, where char gasification occurs by reaction with steam and oxygen while the accompanying ash melts and is removed as slag. The small amount of char and ash particles still accompanying the gases after passing through the cyclones and hot precipitator is removed by two wet scrubbers followed by a cold electrostatic precipitator. All the ammonia and part of the hydrogen sulfide present are also removed by the scrubbers.

The next treatment step concerns the removal of acid gases (carbon dioxide and hydrogen sulfide). A physical solvent process removes these gases from the main stream, then, on selective regeneration, releases a stream of hydrogen sulfide containing part of the carbon dioxide. The hydrogen sulfide stream is sent to the sulfur recovery plant. The carbon dioxide stream is vented to the air together with very small amounts of carbon monoxide and hydrogen sulfide.

The sulfur recovery plant oxidizes 95 percent of the hydrogen sulfide to high-purity elemental sulfur. The remaining 5 percent is present in the tail gas, which is treated in a tail gas unit where all sulfur species are reduced to hydrogen sulfide, then absorbed by an alkaline solution, and oxidized to also give high-purity sulfur. The final vent gas contains carbon dioxide plus traces of carbon oxysulfide, hydrogen sulfide, and carbon monoxide. The sulfur balance for the plant is detailed in Table 1; a total of 98 percent of the coal sulfur content is recovered as elemental sulfur.

The purified gas is now suitable for conversion to hydrocarbon fuels in a Fischer-Tropsch reactor. Carbon dioxide generated at the same time is removed by absorption in a caustic solution and is then vented to the air on regenera-

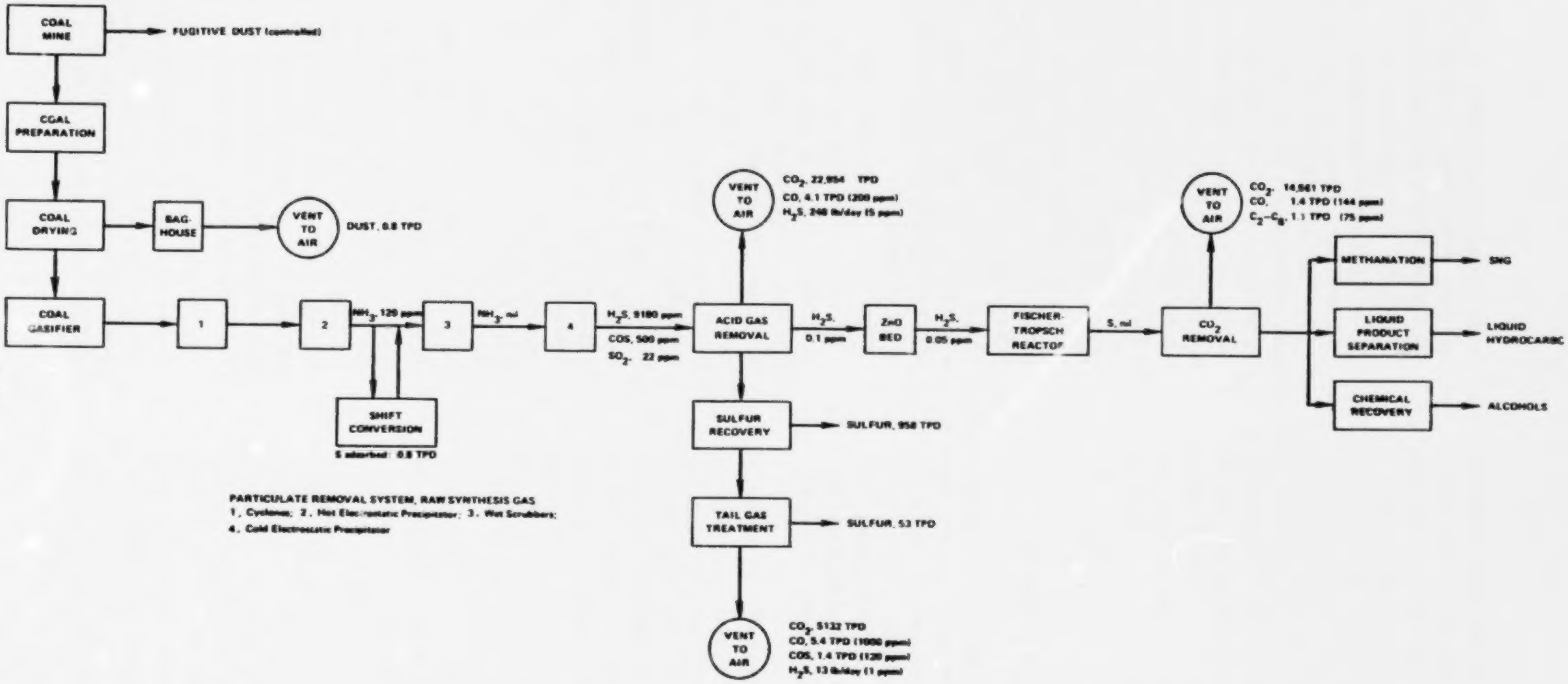
COAL MINE
FUGITIVE DUST (controlled)
COAL PREPARATION
COAL DRYING
BAG-HOUSE
VENT TO AIR
DUST, 0.8 TPD
COAL GASIFIER
1
2
NH_3, 120 ppm
3
NH_3, nil
4
SHIFT CONVERSION
S adsorbed: 0.8 TPD
PARTICULATE REMOVAL SYSTEM, RAW SYNTHESIS GAS
1, Cyclones; 2, Hot Electrostatic Precipitator; 3, Wet Scrubbers;
4, Cold Electrostatic Precipitator
H_2S, 9180 ppm
COS, 500 ppm
SO_2, 22 ppm
ACID GAS REMOVAL
VENT TO AIR
CO_2, 22,954 TPD
CO, 4.1 TPD (200 ppm)
H_2S, 240 lb/day (5 ppm)
SULFUR RECOVERY
SULFUR, 958 TPD
TAIL GAS TREATMENT
SULFUR, 53 TPD
VENT TO AIR
CO_2, 5132 TPD
CO, 5.4 TPD (1000 ppm)
COS, 1.4 TPD (120 ppm)
H_2S, 13 lb/day (1 ppm)
H_2S, 0.1 ppm
ZnO BED
H_2S, 0.05 ppm
FISCHER-TROPSCH REACTOR
S, nil
CO_2 REMOVAL
VENT TO AIR
CO_2, 14,561 TPD
CO, 1.4 TPD (144 ppm)
C_2–C_6, 1.1 TPD (75 ppm)
METHANATION
SNG
LIQUID PRODUCT SEPARATION
LIQUID HYDROCARBC
CHEMICAL RECOVERY
ALCOHOLS

Figure 3. Block flow diagram, air pollution abatement, Fischer-Tropsch plant (1 TPD = 0.9 MgPD)

TABLE 1
SULFUR BALANCE

Sulfur Contributions	MgPD	TPD
Total Input from the Typical Feed Coal	925.3	1,020.0
Outputs: As Elemental Sulfur from Coal Gasifier Gas	917.5	1,011.4
As Reduced Sulfur Emissions (19% H_2S, 81% COS)	0.7	0.8
As Sulfur Dioxide Emissions (actually emitted every six months on regeneration of the shift catalyst)	0.7	0.8
In the Ash	6.4	7.0
	925.3	1,020.0

tion of the absorbent. The vent stream contains traces of carbon monoxide together with traces of light boiling hydrocarbons and methane (a nonpollutant). The Fischer-Tropsch catalyst absorbs the last traces of sulfur present; therefore, all fuels produced, gaseous and liquid, and the chemical byproducts (alcohols) contain nil sulfur.

The streams released to the air are combined in a single stack before venting. The overall amounts and concentrations are shown in Table 2.

Source Emission Standards for coal conversion plants have not been issued by the Federal Government. Guidelines for hydrocarbon (100 ppm) and sulfur dioxide (250 ppm) have been proposed by EPA for Lurgi coal gasification plants. These guidelines are not applicable to the Fischer-Tropsch plant because a different technology is utilized; they are, however, met by the plant effluents.

TABLE 2
COMBINED GASEOUS EFFLUENTS

Gaseous Effluent	MgPD	TPD	ppm
Carbon Dioxide	36,688	42,647	–
Carbon Monoxide	9.9	10.9	306
Carbon Oxysulfide	1.3	1.4	18
Organics (C2 – C6 Hydrocarbons)	1.0	1.1	21
Hydrogen Sulfide	0.12	0.13	3

Of the states, only New Mexico has issued specific regulations covering coal gasification plants; these regulations can be considered for illustrative purposes only because the Fischer-Tropsch plant, as conceived, would be located in the U.S. Eastern Interior (coal) Region. The State of Illinois has issued standards for petrochemicals; this technology is somewhat related to a Fischer-Tropsch operation. Federal standards for petroleum refinery sulfur recovery plants have been proposed;[3] Fischer-Tropsch technology utilizes similar sulfur recovery procedures. For illustration purposes only, the Federal, Illinois, and the New Mexico source emission standards are compared in Table 3 with the emissions from the conceptual Fischer-Tropsch coal conversion plant. As shown in the table, all estimated emissions are projected to either meet or be below the standards.

A dispersion modeling study, using average atmospheric conditions and the EPA-developed PTMAX computer program, was carried out; the results obtained show that the Fischer-Tropsch emissions can meet ambient air quality standards after atmospheric dispersion.

As shown in Table 2, significant carbon dioxide emissions would be generated by the Fischer-Tropsch commercial plant; therefore, it appeared desirable to investigate the possible effects of these emissions. Carbon dioxide is not toxic, and the natural background concentration in the atmosphere has been estimated at 300 to 500 ppm.

Global weather modification effects have been attributed to increased carbon dioxide generation by fossil-fuel combustion. A gradual warming trend on the order of 0.5° C in 25 years has been predicted; however, actual temperature trends have shown a cooling of 0.3° C from 1945 to the present.

On a localized scale, no micrometeorological effects due to increased carbon dioxide have been reported. Emissions from the Fischer-Tropsch facility could approximately double the average atmospheric carbon dioxide concentra-

TABLE 3

COMPARISON OF GASEOUS EMISSIONS WITH FEDERAL, ILLINOIS, AND NEW MEXICO SOURCE EMISSION STANDARDS

(State standards are expressed in the units issued. 1 lb = 453.6 g; 1 gr = 64.8 mg; 1 Btu = 1055 J;

1 ft^3 = 0.028 m^3; MM — million; HHV = higher heating value; L — lower.)

Pollutant	Federal Standards, Petroleum Refinery Sulfur Recovery Plant	Illinois Standards, Petrochemical Plant	New Mexico Standards, Coal Gasification Plant	Gaseous Effluents, Fischer-Tropsch Plant
Particulate Matter	–	78 lb/hr	0.03 gr/ft^3	67 lb/hr[a], 0.03 gr/ft^3
Sulfur Dioxide	250 ppm	1.2 lb/MM Btu	–	Nil[b]
Carbon Monoxide	–	200 ppm, 50% xs air	–	164 ppm[c]
Nitrogen Oxides	–	0.7 lb/MM Btu	–	Nil
Organics (methane excluded)	–	100 ppm (CH_4 equivalent)	–	55 ppm
Total Reduced Sulfur ($H_2S + COS + CS_2$)	300 ppm	–	100 ppm	21 ppm
Hydrogen Sulfide	10 ppm	–	10 ppm	3 ppm
Hydrogen Cyanide	–	–	10 ppm	Nil
Hydrogen Chloride/ Hydrochloric Acid	–	–	5 ppm	Nil
Ammonia	–	–	25 ppm	Nil
Gas Burning Process Boilers, Particulate Matter	–	–	0.03 lb/MM Btu, LHV	–[d]
Gas Burning Process Boilers, Sulfur Dioxide	–	–	0.16 lb/MM Btu, LHV	–[d]
Total Sulfur	–	–	0.008 lb/MM Btu of feed	0.003 lb/MM Btu[e]

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[a] From coal-drying plant.

[b] 47.4 tons of sulfur dioxide emitted twice a year, over 24-48 hours, on regeneration of the catalyst of each shift reactor (six reactors total). If this value were averaged out over the year, it would correspond to 0.004 lb/MM Btu/day.

[c] Value obtained on application of the 50% excess air correction to the streams originating from the acid gas removal unit and from the sulfur plant.

[d] Not applicable (none included in the design).

[e] Includes the sulfur dioxide emitted occasionally on regeneration of the shift reactor catalyst (see Note[b] above).

tions to 600 to 1000 ppm in the vicinity of the plant. The lowest concentration at which some physiological effects (dyspnea and headache) have been observed is 30,000 ppm; therefore, no effects are expected at the levels mentioned. However, vegetable life has been reported to benefit from increased atmospheric concentrations of carbon dioxide.

AQUEOUS EFFLUENTS

The plant design is based on availability of an adequate supply of water. The wastewater treatment is therefore a combination of recycling and discharge of aqueous effluents. The most heavily contaminated streams are concentrated by evaporation, with residuals undergoing thermal destruction in the coal gasifier. The medium-contaminated streams are purified by oxidation and then reused as makeup for boiler feedwater. The lightly polluted streams are treated to make them acceptable to the environment and then are discharged to a river. The generation and control of aqueous contaminants is outlined in Figure 4, which shows the sources of wastewater (listed on the left-hand side) and their progressive treatment and disposition.

The river water supply provides 2,725 m^3/hr (12,000 gpm) of raw water, which, after purification by settling and sand filtration, is used for cooling water makeup and, after further deionization, for boiler feedwater makeup. Potable and sanitary water is supplied by wells. The water supply from the river is not used for coal sizing and handling (a captive system feeding on a mine-based pond is used for this unit) or for coal grinding and drying, where no wet systems are employed.

One of the major contaminated streams is the sour water generated by the wet scrubbers cleaning the gases produced by the coal gasifier. The major contaminants present are hydrogen sulfide, ammonium sulfide, oil, phenols, thiocyanates, cyanides, and solids (ash and char particles). After removal of any oily materials by extraction, most of the gaseous contaminants (hydrogen sulfide and ammonia) are removed by a reboiler-stripper, and then conveyed to the sulfur plant where the hydrogen sulfide is converted to elemental sulfur and the ammonia is oxidized to nitrogen. The stripped aqueous stream is now treated in an oxidizer with oxygen at high pressure to convert most of the organics present to inorganic gases such as carbon dioxide, nitric oxide, and sulfur dioxide. These are led back to the coal gasifier; the reducing atmosphere prevailing there is expected to reduce nitric acids and sulfur dioxide to nitrogen and hydrogen sulfide. After settling and filtration, the aqueous effluent stream from the oxidizer is deionized and reused as boiler feedwater makeup.

The Fischer-Tropsch reactor produces, besides the desired hydrocarbon fuels, a number of alcohols and organic acids. When the product stream is purified by treating with caustic, a waste stream containing alkaline salts of low-molecular weight organic acids is produced. This stream is combined with the boiler water blowdown and the solids slurry obtained as a residue from the settling of the treated sour water, and then concentrated in a triple-effect evaporator. The evaporator condensate is used for boiler feedwater, while the residue is sprayed on the feed coal at the entrance to the coal dryer. A more thorough evaporation occurs in the latter unit; the organic materials are then destroyed when the coal is fed to the gasifier, while the inorganic materials are removed with the ash.

The cooling-tower blowdown stream is the largest in volume, and is only lightly contaminated by corrosion inhibitors (zinc salts and inorganic phosphates) and scale control agents (organic phosphate esters); this stream is mixed with deionizer wastes containing mainly sodium sulfate and other inorganic salts. After neutralization, this stream is treated with lime in a settler-clarifier. The lime sludge, containing most of the zinc and phosphates, is disposed of in a landfill, while the treated stream is returned to the river.

Any oily water streams produced during plant operation are combined with laboratory wastewater, and then passed through a sand filter to coalesce the oil particles. After physical separation of the oil (returned to the gasifier), the aqueous effluent is led to a biopond, where the organic materials present are converted to inorganics by bacterial activity. The biopond

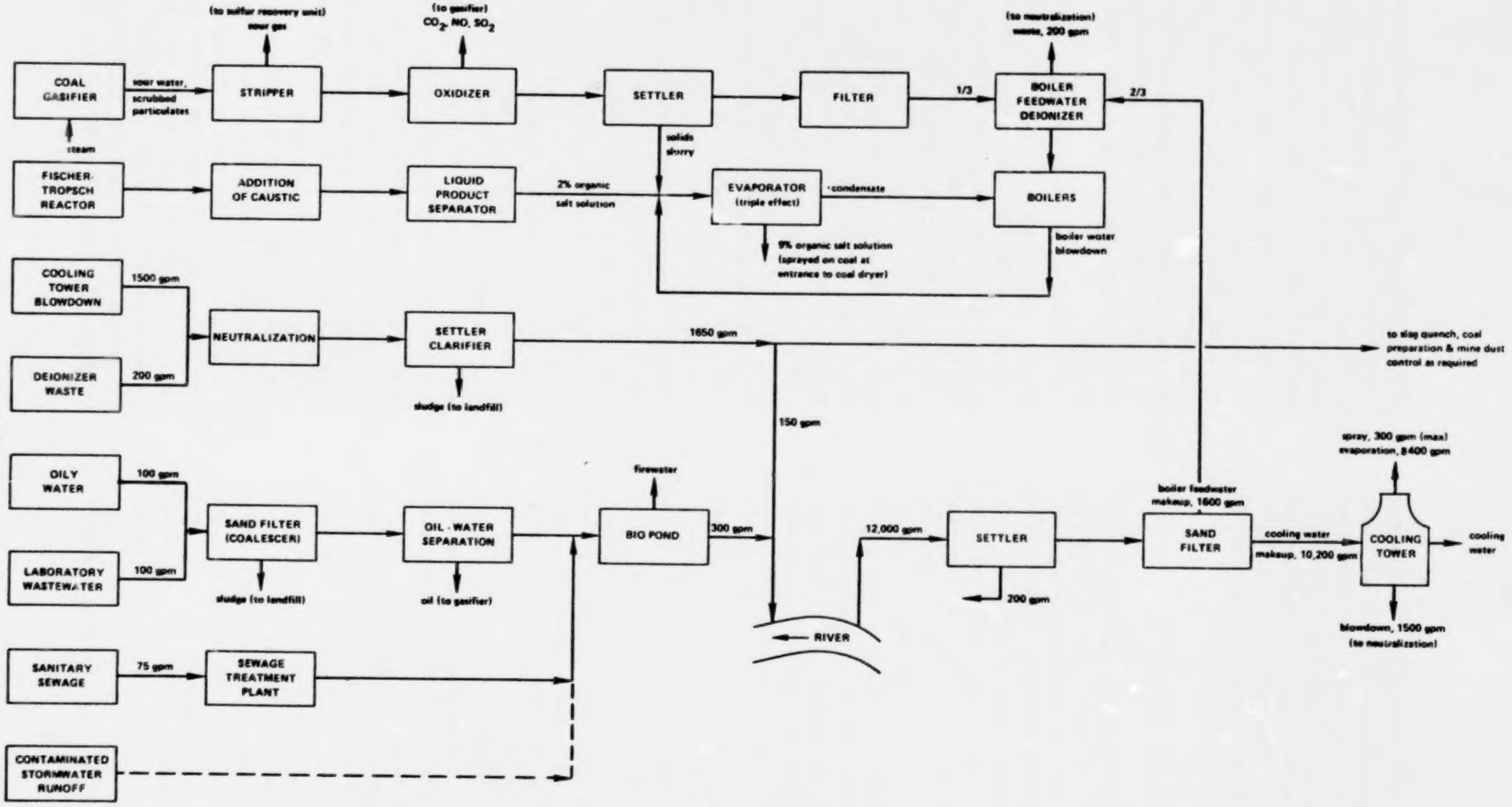
(to sulfur recovery unit)
sour gas
(to gasifier)
CO_2, NO, SO_2
(to neutralization)
waste, 200 gpm
COAL GASIFIER
sour water, scrubbed particulates
steam
STRIPPER
OXIDIZER
SETTLER
FILTER
1/3
BOILER FEEDWATER DEIONIZER
2/3
solids slurry
FISCHER-TROPSCH REACTOR
ADDITION OF CAUSTIC
LIQUID PRODUCT SEPARATOR
2% organic salt solution
EVAPORATOR (triple effect)
condensate
BOILERS
9% organic salt solution (sprayed on coal at entrance to coal dryer)
boiler water blowdown
COOLING TOWER BLOWDOWN
1500 gpm
NEUTRALIZATION
SETTLER CLARIFIER
1650 gpm
to slag quench, coal preparation & mine dust control as required
DEIONIZER WASTE
200 gpm
sludge (to landfill)
150 gpm
OILY WATER
100 gpm
firewater
spray, 300 gpm (max)
evaporation, 8400 gpm
boiler feedwater makeup, 1600 gpm
SAND FILTER (COALESCER)
OIL-WATER SEPARATION
BIO POND
300 gpm
12,000 gpm
SETTLER
SAND FILTER
cooling water
makeup, 10,200 gpm
COOLING TOWER
cooling water
LABORATORY WASTEWATER
100 gpm
sludge (to landfill)
oil (to gasifier)
200 gpm
RIVER
blowdown, 1500 gpm (to neutralization)
SANITARY SEWAGE
75 gpm
SEWAGE TREATMENT PLANT
CONTAMINATED STORMWATER RUNOFF

Figure 4. Block flow diagram, water treatment and supply, Fischer-Tropsch plant (1 gpm = 0.227 m^3/hr)

also receives a minor stream from the sewage-treatment plant, and is used as firewater supply, with any overflow discharged to the river. Strict housekeeping is expected to contain contamination of stormwater to very small volumes; any contaminated water is collected in a stormwater pond (not shown in Figure 4) for subsequent metered feeding to the biopond for treatment.

No aqueous effluent standards specifically addressed to coal conversion plants have been issued by the Federal government or by state legislatures. Standards that are somewhat related to a Fischer-Tropsch process are the Federal standards issued for petroleum refining. Average obtainable concentrations that were the base for such standards are reported in Table 4, together with the corresponding values for the aqueous effluents estimated for the Fischer-Tropsch plant. As shown in the table, these estimated values are either the same or lower than the Federal parameters.[4]

The State of Illinois has issued aqueous effluent standards applicable to all sources discharging to the natural waters of the state. These standards are reported for illustration purposes in Table 5. All Fischer-Tropsch effluents are estimated to either meet, or be lower than such standards.

SOLID WASTES

The Fischer-Tropsch plant generates two main types of solid waste materials: slagged ash from the coal gasifier, and sludges from various wastewater treatment units. All of the ash produced during coal gasification is returned to the bottom of the gasifier together with carbon residues (char); on combustion of the char with oxygen, the temperature produced is sufficient for melting the ash to a slag, which is withdrawn from the bottom of the gasifier. It is estimated that 2132 MgPD (2350 TPD) of slag are produced. On quenching with water, the

TABLE 4

COMPARISON OF AQUEOUS EFFLUENTS WITH FEDERAL PETROLEUM REFINERY STANDARDS*

Parameter	Federal Standards, Petroleum Refinery	Aqueous Effluents, Fischer-Tropsch Plant
BOD 5	15	10
COD	100	100
Total Organic Carbon	33	33
Suspended Solids	10	10
Oil and Grease	5	5
Phenol	0.1	nil
Ammonia-N	80% removal	nil
Sulfide	0.1	nil
Cr. Tertiary	0.25	nil
Cr. Hexavalent	0.005	nil

* Average attainable concentrations from the application of best practicable control technology currently available[4].

TABLE 5

AQUEOUS EFFLUENT STANDARDS, STATE OF ILLINOIS

Constituent	Maximum Concentration (mg/1)
Arsenic (total)	0.25
Barium (total)	2.0
BOD-5	10.0
Cadmium (total)	0.15
Chromium (total hexavalent)	0.3
Chromium (total trivalent)	1.0
Copper (total)	1.0
Cyanide	0.025
Fluoride (total)	15.0
Iron (total)	2.0
Iron (dissolved)	0.5
Lead (total)	0.1
Manganese (total)	1.0
Mercury (total)	0.0005
Nickel (total)	1.0
Oil (hexane solubles or equivalent)	15.0
pH	range 5-10
Phenols	0.3
Selenium (total)	1.0
Silver	0.1
Zinc (total)	1.0
Total Suspended Solids	12.0

slag is fragmented into vitrified granules, which are returned to the mine for burial with the mine spoils. If outlets exist nearby, this material could also be utilized as filler in aggregates for construction blocks or road building.

The sludges from the wastewater treatment units contain mainly inorganic salts, such as calcium and zinc phosphates, which are added to cooling water as corrosion inhibitors. If these sludges were buried with mine spoils, possible contamination of groundwater by zinc could result; they are therefore disposed of in a secure landfill.

The mining and coal cleaning and sizing operations generate sizable amounts of solid wastes which are disposed of at the mine site. The surface mining operation proceeds in an orderly fashion, following an environmentally sound mining plan. The topsoil is removed and stored, then the overburden is stripped and used for refilling of the previous pit, in combination with the inorganic wastes from the coal cleaning and sizing plant (rocks, clay, and mud) and the vitrified ash from the coal gasifier. The mined out area is restored to approximately the original surface contour, then the topsoil is replaced, fertilized, and reseeded, completing the land reclamation cycle.

The coal cleaning and sizing plant is located in proximity of the mine. This arrangement minimizes the exposure to the air of mine spoils, with consequent negligible oxidation of coal pyrites to oxygenated sulfur acids.

FATE OF TRACE ELEMENTS PRESENT IN COAL

Due to its organic origin and its intimate commixture with crustal formations, coal contains a large number of elements in minor or trace quantities. Actually, out of 92 known nontransuranic elements, only 14 (shown in Figure 5) have not yet been found in coal.

Average amounts of trace and other elements for 82 coals from the Eastern Region of the Interior Coal Province are shown in Table 6. These values were developed during a recent study[5] carried out with thorough analytical procedures; the coals analyzed were mainly composite face channel samples.

TABLE 6

MEAN ANALYTICAL VALUES FOR 82 COALS FROM THE ILLINOIS BASIN (FROM REFERENCE 5)*

Constituent	Mean	Constituent	Mean (%)
As	14.91 ppm	Cl	0.15
B	113.79 ppm	Fe	2.06
Be	1.72 ppm	K	0.16
Br	15.27 ppm	Mg	0.05
Cd	2.89 ppm	Na	0.05
Co	9.15 ppm	Si	2.39
Cr	14.10 ppm	Ti	0.06
Cu	14.09 ppm	ORS	1.54
F	59.30 ppm	PYS	1.88
Ga	3.04 ppm	SUS	0.09
Ge	7.51 ppm	TOS	3.51
Hg	0.21 ppm	SXRF	3.19
Mn	53.16 ppm	ADL	7.70
Mo	7.96 ppm	MOIS	10.02
Ni	22.35 ppm	VOL	39.80
P	62.77 ppm	FIXC	48.98
Pb	39.83 ppm	ASH	11.28
Sb	1.35 ppm	Btu/lb	12,748.91
Se	1.99 ppm	C	70.69
Sn	4.56 ppm	H	4.98
V	33.13 ppm	N	1.35
Zn	313.04 ppm	O	8.19
Zr	72.10 ppm	HTA	11.18
Al	1.22 %	LTA	15.22
Ca	0.74 %		

* Abbreviations other than standard chemical symbols: organic sulfur (ORS), pyritic sulfur (PYS), sulfate sulfur (SUS), total sulfur (TOS), sulfur by X-ray fluorescence (SXRF), air-dry loss (ADL), moisture (MOIS), volatile matter (VOL), fixed carbon (FIXC), high-temperature ash (HTA), low-temperature ash (LTA).

A number of studies have analyzed the behavior of trace elements in coal-fired power plants.[6,7] In general, the elements have been divided into two groups, the ones appearing mainly in the bottom ash (elements or oxides having lower volatility) and the ones appearing mainly in the fly ash (elements or oxides having higher volatility). For power plants using dry particulate collection devices (e.g., electrostatic precipitators), it was believed that the

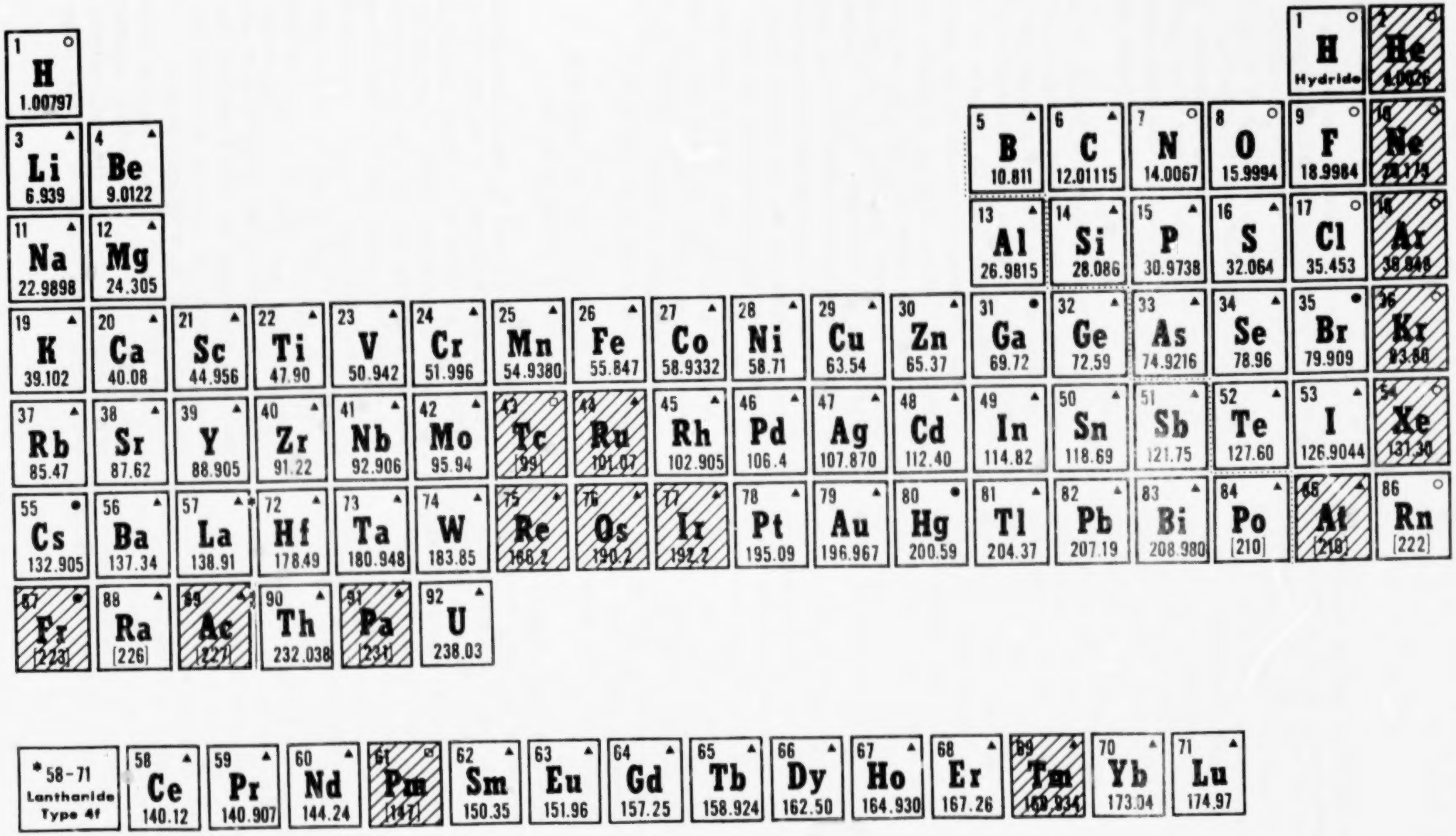

Figure 5. Periodic table of the elements. The elements shaded have NOT been found in coal.

most volatile elements, such as mercury and selenium, could actually escape at the elemental state with the flue gas. Wet scrubbers, however, were believed capable of removing most of the elements from the gas streams and transferring them to the liquid effluent.

Very few data are available for coal conversion plants. A study on trace element disposition for the Sasol (South Africa) facility, reported by the Los Alamos Scientific Laboratory[8] was able to follow the partitioning of trace elements between solid residue (ash), liquid streams, and gases. Among the elements studied, lead, arsenic, and beryllium were found mainly in the ash, selenium and tellurium in the liquid streams, fluorine two-thirds in the ash and one-third in the liquids. Mercury was found present in all phases, but concentrated mainly in the gas; however, 50 percent of the mercury and 17 percent of the beryllium could not be accounted for.

The possibility of leaching of trace metals from the ash into ground or surface waters has been questioned. Experimental studies have been carried out on the leaching of power plant fly ash or unslagged bottom ash;[9] the studies showed that selenium, chromium, and boron, and occasionally mercury and barium, were released on simulated leaching, and the concentrations reached exceeded the values recommended by EPA for public water supplies.

An on-going study at the University of Montana[10] is investigating leaching of trace elements from solid residues of coal conversion plants under neutral, acidic, and basic conditions. Preliminary results indicate that manganese, mercury, and nickel are occasionally released in amounts exceeding recommended potable water standards. The study is hampered by the unavailability of typical residue specimens.

In the Fischer-Tropsch process, essentially nil particulates from coal combustion escape into the atmosphere. Particulate streams, wet or dry, are returned to the bottom of the gasifier, where ash and salts melt and are removed as slag. Any eventual dispersion of the elements present in the slag depends on the possibility of leaching. Possibly, slagged ash features a glass matrix which would inhibit leaching. Leaching experiments using the slag generated by a slagging gasifier, such as the Bi-Gas pilot plant or a Koppers-Totzek unit, would be very useful.

The major concern, therefore, is to identify trace elements which may be occurring in the gaseous state. The reducing atmosphere present in the middle and top part of the gasifier may also favor different combinations, absent in the oxidizing atmosphere of a power plant boiler.

Among the trace elements present in coal with recognized toxic properties, high volatility elements (beryllium, mercury, and lead), do not form gaseous hydrides, will condense on cooling, and will very likely be removed by the aqueous condensates formed in gas cooling and/or purification. Arsenic, antimony, and selenium have lower volatility but can form gaseous (covalent) hydrides: arsine, stibine, and hydrogen selenide. These hydrides however, have stability characteristics which preclude their formation at the temperature and pressure prevailing in the Fischer-Tropsch gasifier. From general chemical principles, it would appear, therefore, that harmful trace elements are not released to the atmosphere. Experimental confirmation, however, is desirable, especially for mercury, and should be obtained from specific pilot plant studies.

FORMATION AND DESTRUCTION OF METAL CARBONYLS

Metal carbonyls form by reaction of carbon monoxide with free metals in the 40-300° C (100-570° F) temperature range. Carbonyls form with all transition metals; nickel, cobalt, and iron carbonyls are most significant since the metals from which they are derived are used as catalysts or for structural equipment.[11,12] Higher pressures [of the order of 100 MPa (15,000 psi)] and the presence of hydrogen favor their formation, while oxygen represses it. They decompose readily in air with half-lives estimated at 10-15 seconds for cobalt carbonyl, 10 minutes for nickel carbonyl, and a few hours for iron carbonyl.

These carbonyls are volatile liquids at room temperature. They all exhibit toxicity, directed at the respiratory system. The most harmful among the three carbonyls is the nickel

TABLE 7

SUGGESTED EXPOSURE GUIDELINES FOR METAL CARBONYLS (FROM REFERENCE 11)

	Air Concentration (ppm)	
Metal Carbonyl	Single Short Term Exposure	Eight-Hour Day
$Ni(CO)_4$	0.04	0.001
$Co(CO)_x + CoH(CO)_4$	0.10	–
$Fe(CO)_5$	0.10	0.01

derivative; for this carbonyl only, chronic effects and carcinogenic activity have been observed. Suggested exposure guidelines and chemical formulas are reported in Table 7.

Iron, nickel, and cobalt catalysts are used in the Fischer-Trosch process, and low carbon steel is employed for structural equipment. However, at the relatively low pressures and high temperatures prevailing, nil metal carbonyls are expected to be formed. In shutdown operations, however, conditions under which metal carbonyls can form may be experienced for short periods of time. In these cases the normal safe practice of flaring vent streams, along with operation of all contaminant removal systems, will prevent release of carbonyls to the atmosphere. Plant personnel who may be entering vessels or handling catalysts, however, will need to be trained in the proper procedures and supplied with adequate protective equipment to safeguard their health.

FORMATION, PARTITION, AND DISPOSITION OF CYANIDE

The question of the generation of cyanide, a highly toxic ion, and of its possible release to the environment, was explored for the Fischer-Tropsch process. Under the chemical and physical conditions experienced in the coal gasifier, nearly all of the nitrogen content of the coal is converted to molecular nitrogen. The remainder is distributed between ammonia and hydrogen cyanide, according to an equilibrium relationship.

This relationship was investigated using a Parsons-modified computer program for the calculation of complex chemical equilibrium compositions, originally developed by NASA[13] for aerospace applications. The equilibrium calculations were made over the 930° C (1700° F, upper stage) to 1650° C (3000° F, lower stage) temperature range and at the 3.5 MPa (500 psia) pressure which are representative of the conditions expected in the gasifier. The equilibria considered involved a series of molecular and ionic components compatible with the elemental analysis of the charge to the gasifier and with the probability of their occurrence in the effluent gas.

The results obtained, plotted in Figure 6, show that very small amounts of cyanide, of the order of 0.7 mole/hour, are produced at the outlet temperature (930° C, 1700° F) of the gasifier. Even if complete equilibrium were not achieved but were equivalent for example to that calculated for 1100° C (2000° F), the quantities of cyanide in the gases would still be quite small.

When the effluent gas undergoes wet scrubbing, most of the cyanide remains in the gas

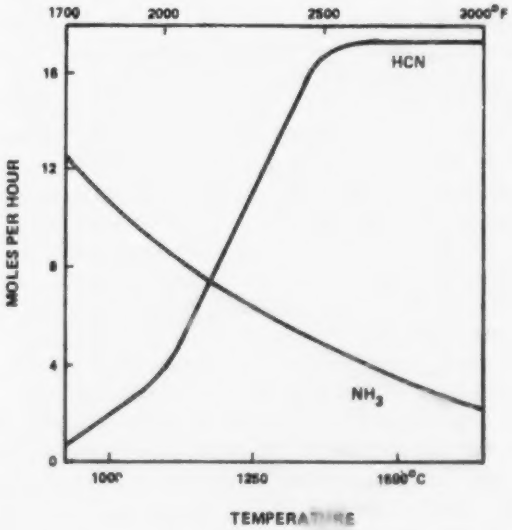

Figure 6. Ammonia-cyanide equilibria.

stream because the sour water generated is only slightly alkaline. It is then absorbed, together with hydrogen sulfide, by the physical solvent process; on regeneration, it is conveyed to the sulfur recovery plant, where it undergoes thermal oxidation to nitrogen and carbon dioxide. The cyanide fraction which had remained in the aqueous stream is treated, together with other organics, with oxygen at high pressure in the oxidizer unit; there these compounds are converted to inorganic gases such as carbon dioxide and nitric oxide. These are led back to the coal gasifier, where under the prevailing reducing conditions nitric oxide is expected to be reduced to nitrogen.

It appears therefore that very little cyanide is generated, and any amounts produced are destroyed within the Fischer-Tropsch process, so that nil cyanide is released to the environment.

FORMATION OF COAL TAR CARCINOGENS AND BIOHAZARDS INVOLVED

Of particular interest in coal conversion projects is the possible formation of carcinogenic compounds on hydrogenation and pyrolysis of coal. These compounds are polynuclear aromatic hydrocarbons and heterocyclics usually found in coal tar. Nil coal oils and coal tars are expected to be produced under the operating conditions of the entrained coal gasifier used in the Fischer-Tropsch plant.

Carcinogenic activity for laboratory animals has been observed for distillation residuals obtained from petroleum refining.[14] Similar fractions are obtained on distillation of the liquid hydrocarbons produced by the Fischer-Tropsch reactor, and Fischer-Tropsch oils boiling above 250° C (480° F) were found carcinogenic in mice.[15] However, the carcinogenic activity is much smaller than observed for coal tar products because Fischer-Tropsch fuels consist essentially of aliphatic compounds. Crudes also contain less aromatics than coal oils and tars; the refining process occurs in close systems, so that very little contact of workers with products occurs; equipment handling residual oil is often color coded, so that workers are warned to avoid direct contact. As a consequence, cancer frequency in oil refinery workers is the same as for other industrial occupations. Equally efficient occupational safety procedures will be maintained in Fischer-Tropsch operations, thereby minimizing any environmental risks.

ACKNOWLEDGEMENT

We gratefully acknowledge the support and guidance of ERDA-FE in our work, and the contribution of the many people at Parsons who participate in coal conversion activities.

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CONTROL TECHNOLOGY DEVELOPMENT FOR FUEL CONVERSION SYSTEM WASTES

Louis E. Bostwick
Pullman Kellogg
a Division of Pullman Incorporated
Houston, Texas

Abstract

Pullman Kellogg's contract with the Environmental Protection Agency concerns control technology development for fuel conversion system waste utilization and disposal, for coal storage, preparation, and feeding, and for wastewater treatment. The program includes assessment of available and developing control technology as applied to fuel conversion effluents/emissions/wastes and relationship to present and proposed environmental regulations, continues with theoretical and experimental development of promising alternate control technologies, then concludes with an overall comparative analysis of all technologies and an engineering design and cost estimate for those control methods judged to be appropriate for integration into conversion system flow schemes.

Since the program has been operating for only five of its scheduled 36 months, this paper may be considered as a progress and planning report.

Pullman Kellogg's contract with EPA has as its objective the development of control technology for fuel conversion system waste utilization and disposal, for coal storage, preparation, and feeding, and for wastewater treatment. The 36-month project involves assessment of available and developing control technology, development of control technology and evaluation of control technology. The work is designed to interface with other studies in the EPA synthetic fuels program for interchange of information and definition of problems.

THE PROJECT PROGRAM

The program began in April 1977 with literature searches and data surveys directed toward definition of the emission streams in fuel conversion processes by quantity and composition, assessment of available and developing control technology and identification of existing and proposed environmental requirements. The results of these efforts are the base for the steps of the program that follow:

1. *Projection of new or more stringent environmental standards.*
   Hazardous or environmentally dangerous constituents of conversion plant waste streams are evaluated and new or more stringent regulations are projected with emphasis on health effects, land use considerations and geography. These criteria serve as guides for development of control technology.
2. *Identification of control needs.*
   Controls required to meet existing and proposed standards and criteria for conversion processes are determined by comparison of the pollutant standard with effluents from available or developing control processes. Areas requiring better control technology are then defined.
3. *Identification of new data needs.*
   Comparison of the review of control technology with the identification of control needs defines the areas in which data are insufficient or unavailable for assessment of needs for available technology or control methods.
4. *Field data acquisition.*
   Data to at least partially fill the gaps defined as new data needs are gathered during field trips to observe control processes in fuel conversion processes or in similar control processes in other industries. Compositions and quantities of emissions streams are determined and sampling and analysis of control process influent and effluent streams are accomplished.
5. *Economic analysis of available and developing control technology.*
   Capital and operating costs for individual control processes are determined and then used to predict costs for environmental control for fuel conversion processes.

6. *Program emphasis for development of control technology.*
   In accordance with the overall EPA objectives, a multiyear control technology development plan is formulated, time-phased to coincide with fuel conversion technology development.
7. *Evaluation of alternate control technology.*
   Theoretical studies of control technology that are available in the literature are reviewed for mechanisms that show promise and might be developed for areas where new technology is needed. Assembly of conceptual flow diagrams of promising control routes is followed by cost evaluations and comparison of proposed processes with existing processes. With consideration of the program emphasis philosophy, the field of new processes is narrowed to those most attractive, technically and economically, for further development.
8. *Laboratory and bench-scale development.*
   Accurate definition of objectives and analysis of means of attaining the objectives leads to formulation of a program for experimentation to establish conditions of operations required to achieve the desired level of control. The laboratory work is seen as a screening mechanism to establish the range of control process operations which aids in selection of operating methods for bench-scale development.
9. *Integration of process with needed control technology.*
   This check point ensures that processes under development in the laboratory fit the specific situations they are intended to control. New laboratory data are compared with the concepts developed during evaluation of promising alternate technology.
10. *Overall comparative analysis of control processes.*
    Existing available control processes, as required by fuel conversion processes, are compared according to costs, level of control, applicability and other advantages and disadvantages. After laboratory and bench work are complete, promising developing control technology is evaluated by the same criteria and with such additional considerations as costs of remaining development programs and risks.
11. *Design preparation.*
    Several control processes are selected from the results of the overall comparative analysis and capital investment and operating costs are developed for each complete control process.

PROGRESS IN THE PROGRAM

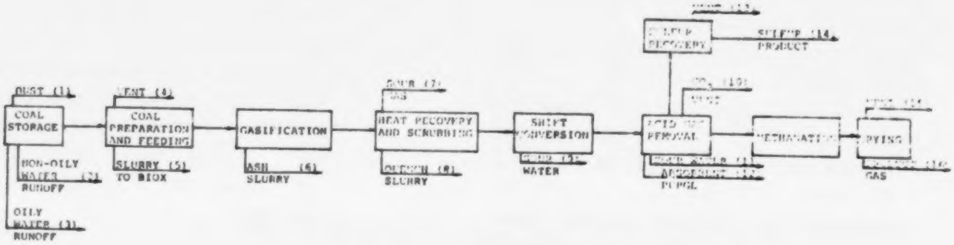
Literature Search for Conversion Process Information

As originally conceived, information on the quantities and compositions of the effluents and wastes from each coal conversion process would be collected and grouped as solid, liquid, or gas in order to define the areas for application of control technology. However, a lack of useable information on conversion process emissions became apparent very early in the survey of published reports and articles concerning the processes because the emphasis in development of conversion processes had been almost entirely on the processes themselves and much less attention had been given to collecting data on their emissions. Some small amount of information was published on emissions, derived mainly from laboratory and bench-scale process development work, and some information was available in reports on conceptual conversion process designs, but the total was insufficient for definition of required control technology. The problem was compounded by the one- to two-year time interval between completion of a report of work on a particular process and its publication and procurement.

Literature searches were conducted through EPA, NTIS, and Chemical Abstracts data banks and the microfiche library of Oak Ridge National Laboratory reports at Rice University in Houston. The search continues through weekly monitoring of NTIS abstracts and Chemical Abstracts for the life of the project.

TABLE 1

AVAILABLE INFORMATION ON EMISSIONS FROM COAL GASIFICATION PROCESSES

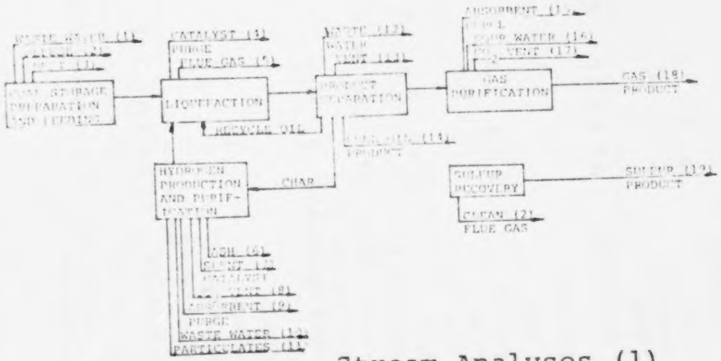

DUST (1)
COAL STORAGE
NON-OILY WATER (2) RUNOFF
OILY WATER (3) RUNOFF
VENT (4)
COAL PREPARATION AND FEEDING
SLURRY (5) TO BIOX
GASIFICATION
ASH (6) SLURRY
SOUR (7) GAS
HEAT RECOVERY AND SCRUBBING
QUENCH (8) SLURRY
SHIFT CONVERSION
WATER
SULFUR RECOVERY
SULFUR (14) PRODUCT
CO_2 (10)
ACID GAS REMOVAL
PURGE
GAS

	Stream Analyses (1)															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
CO_2 Acceptor					P	A	A	A			A				A	A
Synthane				A	P	A		A	A						A	
HyGas (Steam/Ox.)						P		A	A	Q			Q		A	A
HyGas (Steam/Iron)				A	A	P		P	A		A		Q		A	A
Lurgi (Dry Ash)					P	P	A	A		Q			Q		Q	A
Lurgi (Slag Ash) (2)																
Bi-Gas						P		P	P				P	P	P	P
Battelle Agglomerating Ash (3)																
COGAS (4)																
Hydrane						A										A
Koppers-Totzek						A		A								A
Winkler				A		P										A
Westinghouse (15)																
Foster Wheeler (6)																
AI Molten Salt (7)																A
Combustion Engineering (8)						Q										Q
Riley-Morgan						P			P							A
Wellman-Galusha									P							A
U-Gas				Q		A			Q				Q			A
Babcock & Wilcox (9)				A				A				A	A			
ERDA/MERC (10)																
Texaco (2)																
BCR (11)																
Woodall-Duckham (12)																

(1) A = Analysis, either real or conceptual; P = Partial analysis; Q = Quantities only.
(2) Proprietary. No data released to date. Possible future release.
(3) PDU operation expected late 1977. Effluent data available possibly in early 1978.
(4) Development mostly proprietary, very little effluent data. Now being evaluated by ERDA vs. Slagging Lurgi.
(5) Emphasizes turbine development. Little effluent data available.
(6) Conceptual design only. No data. Used Bi-Gas gasifier.
(7) PDU scheduled for 1978-9 operation. Very limited data mostly on process.
(8) Pilot plant effluent data expected in six-twelve months.
(9) Will not be built. Bi-Gas is very similar and was built by B&W.
(10) Process development with no published effluent data.
(11) Pilot Plant. No effluent data.
(12) Commercial operation. No published effluent data.

TABLE 2

AVAILABLE INFORMATION ON EMISSIONS FROM COAL LIQUEFACTION PROCESSES


WASTE WATER (1)
COAL STORAGE PREPARATION AND FEEDING
CATALYST (4)
PURGE
FLUE GAS (5)
LIQUEFACTION
RECYCLE OIL
WASTE WATER (12)
VENT (13)
PRODUCT SEPARATION
FUEL OIL (14) PRODUCT
ABSORBENT (15)
SOUR WATER (16)
VENT (17)
GAS PURIFICATION
GAS (18) PRODUCT
HYDROGEN PRODUCTION AND PURIFICATION
CHAR
SULFUR RECOVERY
SULFUR (19) PRODUCT
CLEAN (20) FLUE GAS
ASH (6)
SPENT (7) CATALYST
VENT (8)
ABSORBENT (9)
PURGE
WASTE WATER (10)
PARTICULATES (11)

	Stream Analyses (1)																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
COED (2)	P	Q				P		Q		A		A		Q		A			Q	A
Clean Coke (3)																		Q		
SRC (4)			Q			Q								P			A	P	Q	A
H-Coal (5)				Q								Q		P				Q	Q	
Synthoil (6)						A						Q		A				Q	Q	
Donor Solvent (7)																				

(1) A = Analysis, either real or conceptual; P = Partial analysis; Q = Quantities only.

(2) Information from conceptual design for COED combined with COGAS.

(3) No published effluent information to date. Data expected by end of 1977.

(4) Information from conceptual design of SRC II process.

(5) Pilot plant construction to be completed in 1978, operation scheduled into 1980.

(6) PDU operation to start in 1978.

(7) No published effluent information to date. Environmental Assessment scheduled for late 1977 completion.

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Results of the Literature Search for Conversion Process Information

The literature searches were supplemented by direct contact with conversion process developers or with ERDA, whichever was applicable, to ascertain process status and availability of reports that would contain emissions data. The results of the data search are summarized in Table 1 for gasification processes and Table 2 for liquefaction processes. The data gaps, the status of the processes and the projections for process development in the future emphasize the validity of one of the basic concepts of the Fuel Process Branch of EPA: that the level of environmental concern may be relatively low during the initial investigations of promising fuel conversion processes and should increase to comprehensive programs as the conversion processes are developed during the pilot plant and larger operations. Thus, lack of published emissions data on a relatively new, bench-scale process is understandable and is not a cause of great concern for the moment. Lack of any plans for gathering emissions data from a process, or lack of access to any data that may be reported, are both causes for concern from the standpoints of being aware of progress of development of the conversion process and of outlining for special attention any unusual emissions problems. For these reasons, efforts in monitoring literature and in maintaining contacts with process developers are planned as a continuous update of emissions information through the project.

Gasification Process Categorization

The premise that conversion processes fed with the same coal and operating under the same or similar conditions will have the same or similar emissions has been applied to the coal gasification processes. The groupings that result allow application of emissions information among processes within each group in order to close the information gaps.

Coal gasification processes were divided into "clean" processes, in which little or no oils, tars, and phenols are produced, and "dirty" processes that produce oils, tars, and phenols. The effect of the grouping on the availability of data within the group is shown in Table 3.

TABLE 3

CATEGORIZATION OF COAL GASIFICATION PROCESSES

Clean Processes	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
CO_2 Acceptor					P	A	A	A			A				A	A
Bi-Gas						P		P	P				P	P	P	P
Koppers-Totzek						A		A								A
Winkler				A		P										A
Westinghouse																
Foster Wheeler																
Combustion Engineering						Q										Q
U-Gas				Q		A			Q				Q			A
Babcock & Wilcox				A				A				A	A			
CONSENSUS				A	P	A	A	A	P		A	A	A	P	A	A
Dirty Processes																
Synthane				A	P	A		A	A						A	
HyGas (Steam/Ox.)						P		A	A				Q		A	A
HyGas (Steam/Iron)				A	A	P		P	A		A		Q		A	A
Lurgi (Dry Ash)					P	P	A	A		Q			Q		Q	A
Lurgi (Slag Ash)																
Battelle Agglomerating Ash						P		P	P				P	P	P	P
COGAS																
Hydrane						A										A
Riley Morgan						P			P							A
Wellman-Galusha									P							A
CONSENSUS				A	A	A	A	A	A	Q	A		P	P	A	A

*A = Analyses, either real or conceptual; P = Partial analysis; Q = Quantities only.

Classifying gasification processes according to their production of oils, tars, and phenols is useful because these components eventually appear in the waste water streams. Their presence requires the use of additional treatment units (for example, biological oxidation or phenol recovery) while their absence means significantly less intense water treatment will be needed. In addition, production of these contaminants generally reflects gasifier operating conditions, which in turn determine the form of solid waste produced (slag or dry ash).

Oils, tars, and phenols may be formed during the gasification of coal. However, by increasing the gasifier temperature, the residence time or the average bed temperature (by operating in the entrained flow mode or injecting the coal feed into the hot bottom part of the gasifier), production of oils, tars, and phenols is reduced or eliminated.

It is noteworthy that the "clean" processes have either entrained-flow or fluidized-bed gasifiers operating at temperatures of 1900° F or higher and produce ash as a slag or as agglomerates. In contrast, the "dirty" processes have either fixed bed or fluidized-bed gasifiers operating at temperatures below 1900° F.

There are several exceptions to the generalization. The CO_2 Acceptor gasifier operates at less than 1900° F but is "clean" because the gasifier design provides for long residence time. The Winkler gasifier also operates at less than 1900° F but is "clean" because the feed coal is injected into the bottom of the gasifier to yield a higher average bed temperature. Not much is known at this time concerning the Battelle Agglomerating Ash Process, however, sources indicate that no tars or oils are produced but that some heavy inorganics may be present.[1] The Al Molten Salt Process is a special case in that no oils, tars, or phenols are produced, but the reaction system may produce effluents significantly different from the other gasification processes.

From the consensus of each of the process groups a first approximation of the quantities and concentrations of emission streams may be deduced. Used with caution, the deductions will serve as a basis for evaluation of the efficiency of the application of available and developing control technology to the pollutants by comparison with existing and proposed environmental standards and criteria for emissions from conversion plants.

The weaknesses in the categorization method for deduction of emission stream quantities and compositions are apparent. Strengthening of the information is needed to make as firm as practicable the foundation for the subsequent steps of the program. Therefore, plans have been formulated for monitoring literature and implementing personal contacts to gather and correlate data as developed on the processes that are developing rapidly and that offer the most promise for generating useable effluent data:

CO_2 Acceptor (Clean, High-Btu)
Koppers-Totzek and/or Winkler (Clean, Low, or Medium-Btu)
Synthane, Lurgi and HyGas (Dirty, High-Btu)
Riley-Morgan and Wellman-Galusha (Dirty, Low-Btu)

Liquefaction Process Categorization

Grouping of coal liquefaction processes according to operating conditions in order to deduce the composition and quantity of each emission stream was not as successful as with coal gasification processes due to lack of meaningful data. As a first approximation, the processes were separated into two groups:

	Process	Temperature	Pressure	Phase*
Group 1:	Pyrolysis/Hydrocarbonization			
	COED	550-1500°F	8 psig	S,G
	Clean Coke	880-900	150	S,G
Group 2:	Solvent Hydrogenation			
	SRC	800-900°F	1500	L,S,G
	H-Coal	850	2000-4000	L,S,G
	Donor Solvent	700-900	1450-2450	L,S
	Synthoil	850	2000-4000	L,S,G

*L = Liquid; S = Solid; G = Gas

In general, coal liquefaction processes are more nearly alike than are coal gasification processes. For example, since all liquefaction processes produce hydrocarbon liquids, it is inevitable that there will be effluent streams containing tars, phenols, and oils and that these streams will require effluent control systems similar to those applicable to the fixed bed ("dirty") gasification processes.

Hydrogen for coal liquefaction can be generated either by light hydrocarbon reforming or by gasification of residue/char. The general statement may be made that hydrogen production by similar methods yields similar effluents and requires similar control methods for that process step.

---

[1] It should be noted that "heavy inorganics" are present in *all* processes due volatility of such components in the coal, e.g., Cd, Zn, Cl, Hg, F, As, etc. Also nitrogen compounds in the coal will appear as ammonia and cyanides/cyanates in *all* processes.

In Group 1, the byproduct char from the COED process is gasified to produce hydrogen and fuel gas. Studies on the gasification of the char have led to the development of the COGAS process, and COGAS now includes COED. The Clean Coke process produces a coke substitute from the byproduct char. Both processes use low-pressure staged fluid bed reactors to pyrolyze/hydrocarbonize coal into char and oil.

The processes in Group 2 liquefy coal by combining it with a recycle oil stream to form a slurry, adding hydrogen and heating the mixture at high pressure to yield oil and a residue of undissolved coal and ash. SRC does not use a catalyst. Donor Solvent catalytically hydrogenates the recycle solvent. H-Coal and Synthoil use a catalyst in the liquefaction reactor. The residue may be disposed of by combustion, coking or gasification.

An attempt to utilize the effect of the grouping on the availability of data within the group is ineffective, due to the lack of data in many areas and the lack of definition of the means of disposal of residue. Monitoring literature and implementation of personal contacts in order to gather and correlate information as it is developed are recognized as being of paramount importance and are being vigorously pursued.

Compilation of Existing and Proposed Environmental Requirements

Environmental regulations, standards, and related restrictions have been collected, organized, reviewed, and synopsized. Sources were State, regional, and Federal publications and, wherever applicable, international agreements. Detailed evaluation was limited to those constituents of effluent, emission, and waste streams which best judgment indicated will be hazardous or environmentally dangerous due to inherent properties or to concentrations. The Multimedia Environmental Goals that are currently under development by IERL-RTP are included in the evaluation, since these establish a concentration for each constituent which estimates a level of concern for assessment purposes.

The draft report of the compilation and evaluation of the environmental requirements is scheduled for completion by the end of September. Monitoring of source material will be a continuing effort through the project.

VOLATILITY OF COAL AND ITS BY-PRODUCTS

By
J. K. Kuhn, D. Kidd, J. Thomas, Jr.,
R. Cahill, D. Dickerson, R. Shiley,
C. Kruse, N. F. Shimp

Illinois State Geological Survey
Urbana, Illinois

Abstract

A number of projects are underway to assess the relationship of trace and minor elements to the volatile and residual products formed during the pyrolysis of coal. Physical and chemical demineralization of coals has shown that, with the exception of organic sulfur, all or nearly all of the trace and minor elements are associated with the mineral matter. Since the minerals cannot be totally removed with current commercial cleaning procedures, their volatility is as important to coal processing as that of the organic constituents.

Internal surface area measurements of coals and the chars produced upon pyrolysis show that the surface area is at a minimum at 350°C to 450°C. At this temperature range, most of the volatile matter has been expelled, and the greatest rate of sulfur loss occurs. The surface area increases (to the original area) above this temperature until the original structure is destroyed at 750°C to 800°C.

Six coals were pyrolyzed at 450°C and 700°C. Significant losses of some trace elements occurred at the lower temperature, whereas only slightly increased loss occurred at the higher temperature. Of the elements determined, S, In, Cl, Sn, Sb, As, Se, and Hg showed considerable volatization, whereas others such as Cd and Zn exhibited a lesser degree of loss.

INTRODUCTION

The volatility of coal and the elements contained in it are of concern both environmentally and economically. The possible release of trace elements during power generation and conversion processes such as liquefaction and gasification may endanger the environment and be deleterious to catalysts in coal conversion.

A large portion of the many elements contained in the mineral matter of coal may be removed by physical cleaning. The determination of the association of these elements with the organic and inorganic portions of coal is necessary to assess the value of pretreatment procedures. Both the physical characteristics of the coal and the mode of occurrence of the elements in coal have significant effects on the volatility of products formed during power generation and conversion. The projects reported here are directed toward finding information that can be used in evaluating problems in coal utilization.

Organically Associated Trace Elements

The type of association or combination in which an element occurs in natural materials can influence its reactivity or volatility. Analyses of fractions of coals obtained by specific gravity methods have produced data showing whether elements are associated with the mineral or the organic fractions of coal. A total separation of the mineral matter from the organic matter cannot be made by gravity methods alone, however. Consequently, we have combined physical and chemical methods to achieve more complete separation. Direct analysis of an almost entirely organic fraction should yield definitive information on those elements that are associated with organic matter. If the amounts of elements are sufficiently large, the volatilities of organically combined trace elements might be determined separately from the volatilities of the mineral elements.

To accomplish this, mineral matter was removed from cleaned coal by means of selective chemical dissolution, in which the coal organic fraction was relatively unaltered. A brief summary of the demineralization procedure follows:

1. Raw coal floated at 1.40 specific gravity
2. 2-hr reflux with 10 percent HNO_3
3. 2-hr digestion with 48 percent HF at 70°C
4. 1-hr digestion with 25 percent HCl at 70° C
5. Vacuum-dry fractions

This procedure may oxidize some of the organic matter; however, any major effect should be indicated by a change in the organic sulfur content. Table 1 shows the extent of elemental extraction over time for major, minor, and trace elements. The values were normalized for loss of weight from removal of mineral matter.

The data show that acid extraction removes most of the mineral phases from coal. Removal of the mineral matter has little or no effect on the organic sulfur content of the coal; thus, we believe that for most coals the organic portion of the coal is nearly unaltered. After extraction, a total trace element concentration (including Si, Al, and others, but excluding S) of only about 250 ppm remains in most coals.

Table 2 shows the mode (the concentration occurring most frequently) and minima and maxima of the concentrations of some major, minor, and trace elements in the 25 raw and chemically cleaned coals studied in this project. In general, results of these analyses have confirmed conclusions drawn from earlier float/sink studies; e.g., Ge, Be, Sb, and Br have high organic associations in coal; Ni, Cu, Cr, and Hg tend to be in both organic and inorganic combinations; and Zn, Cd, As, and Fe are primarily associated with coal mineral matter. Boron is absent in the chemically cleaned coal, but float/sink data indicate that B is associated mainly with the organic fraction of coal. Therefore, we believe the chemical treatment removes B from the organic matter, perhaps as a fluoride.

Results of chemical extraction of mineral matter from coal are in relative agreement with those obtained by gravity separations, except that the concentration levels of most trace elements in the chemically extracted coals (i.e., organically associated trace elements) are significantly lower than those contained in the lighter, organic-rich float fractions from the same coal. This raises the question of which values more nearly represent the organic portions of coal; those in chemically cleaned coals may be low and those in light gravity fractions may be high.

Recently we have compared some of the data on trace elements from chemically cleaned coals with the concentrations of organically combined trace elements estimated from washability and "organic affinity" curves. The following description of the manner in which such values are calculated was taken from *Trace Elements in Coal: Occurrence and Distribution* by Gluskoter et al. (1977). Figure 1 presents both unadjusted (standard) and adjusted, normalized washability curves for zinc in a sample of the Herrin (No. 6) Coal Member. In thestandard (unadjusted) washability curve (Figure 1a), the extrapolated ordinate intercept is approximately 4.5 ppm. The adjusted curve intercepts the ordinate at zero, and the curve reaches the zero zinc value at approximately 90 percent recovery (90 on the abscissa). A portion of the mineral matter estimated to be inseparable has been subtracted from the normal curve to produce the adjusted curve; the adjusted cumulative curve (Figure 1b) was constructed after the value, *F*, was determined, as in the following example for zinc, and subtracted from each of the 5 datum points.

$$F = \frac{LTA(Light)}{LTA(1.60\ \mathrm{S})} \times \mathrm{Zn}(1.60\ \mathrm{S})$$

$$= \frac{6.10}{77.80} \times 250\ \mathrm{ppm}$$

$$= 19.6\ \mathrm{ppm}$$

LTA(Light) is the percentage of low-temperature ash in the lightest float fraction.

LTA(1.60 S) is the percentage of low-temperature ash in 1.60 sink fraction

Zn(1.60 S) is the concentration in 1.60 sink fraction (ppm).

If the value of a datum point was negative after *F* was subtracted from the reported concentration, the value was taken to be zero. A fourth-order polynomial curve was drawn to best fit the data points. Thus, in the case of Zn, the net effect was a general lowering of the curve. The area beneath the curve is proportional to the element's organic affinity, and the intersection of the curve with the vertical axis is an estimate of the Zn concentration associated with organic material.

Tables 3, 4, and 5 are typical examples of element concentrations in raw coals and their respective organic-rich fractions which were

TABLE 1

EFFECT OF PHYSICAL AND CHEMICAL TREATMENT ON THE CONCENTRATIONS OF SOME ELEMENTS IN AN ILLINOIS NO. 6 COAL SAMPLE

	Raw coal		1.40 float		1-hr treatment		2-hr treatment	
Element	%	ppm	%	ppm	%	ppm	%	ppm
Al	1.40		1.08			124		35
Si	3.20		2.15			250		41
Ca	.51		.094			33		25
K	.13		.11			1		1
Na	.04		.027			7		5
Cl	.05		.02			390		390
S	6.45		3.59		2.64		2.52	
Fe	2.60		.90			170		66
Ti	.06		.08			25		11
Organic S	2.55		2.66		2.64		2.52	
P		50		13		9.7		<1.0
As		3.4		2.8		.088		.062
Pb		<.1		<.1		<.1		<.1
Br		3.5		3.4		2.4		2.9
Cu		13		13		3.4		2.1
Ni		24		7.5		2.5		<1
Zn		43		20.5		8.8		4.4
V		36		28		6.1		3.5
Rb		23		10.3		<1		<1
Cs		2.0		.66		<.1		<.01
Ba		54		42		21		3.6
Sr		28		10.3		1.80		1.3
Sc		4.1		2.8		.88		.53
Cr		21		16.8		8.8		6.2
Co		5.5		3.7		.35		.35
Ga		2.4		2.8		.88		.62
Se		4.3		1.4		.18		.26
Sb		.49		.19		.088		.088
Hf		1.1		.46		.088		.088
W		.59		.28		.088		.052
La		6.1		3.4		.88		.61
Ce		25		7.3		1.8		1.5
Sn		.86		.8		.44		.35
Eu		.26		.19		.09		.088
Dy		1.2		.56		.53		.44
Lu		<.02		.02		.03		.02
Yb		.84		.46		.22		.20
Tb		.45		.09		.09		.09
Th		3.6		1.9		.88		.88
U		1.9		.46		.18		.09
Mo		18		3.5		.53		.44
Hg		.23		.066		.044		.044
Mn		60		10.3		.35		.26

NOTE: All values normalized to raw coal.

TABLE 2

MODES, MAXIMA, AND MINIMA OF CONCENTRATIONS OF ELEMENTS FOR 25 RAW AND CHEMICALLY CLEANED COALS

	Raw coal						Mineral-free coal					
	Mode		Maximum		Minimum		Mode		Maximum		Minimum	
Element	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Al	1.10		1.60		.36			41		143		22
Si	2.59		3.47		.71			37		62		26
Ca	.51		3.30		.18			18		57		7
K	.14		.21		.02			4		200		<1
Na	.04		.15		.01			5		25		<1
S	1.43		6.45		.49		.79		2.52		.28	
Organic S	.77		2.52		.25		.79		2.52		.28	
Fe	1.95		2.96		.31			86		110		66
Ti	.06		.08		.02			18		35		2.1
P		50		200		10		4.5		19		<1
As		4		9.4		1.2		.25		.50		.046
Pb		4		56		<.1		.7		1.1		<.1
Mo		14		26		.7		.44		.55		.37
Cu		12		92		2.1		3.4		8.8		.7
Ni		18		29		2.9		2.1		4.6		<1
Zn		46		328		16		4		4.6		<1
V		36		62		5.4		3.5		6.4		2
Ba		78		500		41		10		20.9		2.9
Cr		16		46		6		3		7		.28
Br		15		33		.9		7		24		.1
Mn		42		69		12		.28		.7		.19
Co		7		15		.6		.34		1.5		<.04
Ga		2.4		3.8		.8		.47		1.0		.38
Se		2.0		4.3		1.1		.26		.7		<.1
Sb		.4		2.5		.19		.28		.46		.088
Hg		.14		.23		.06		.055		.060		.044
Sr		32		190		23		4.6		15		<1.3

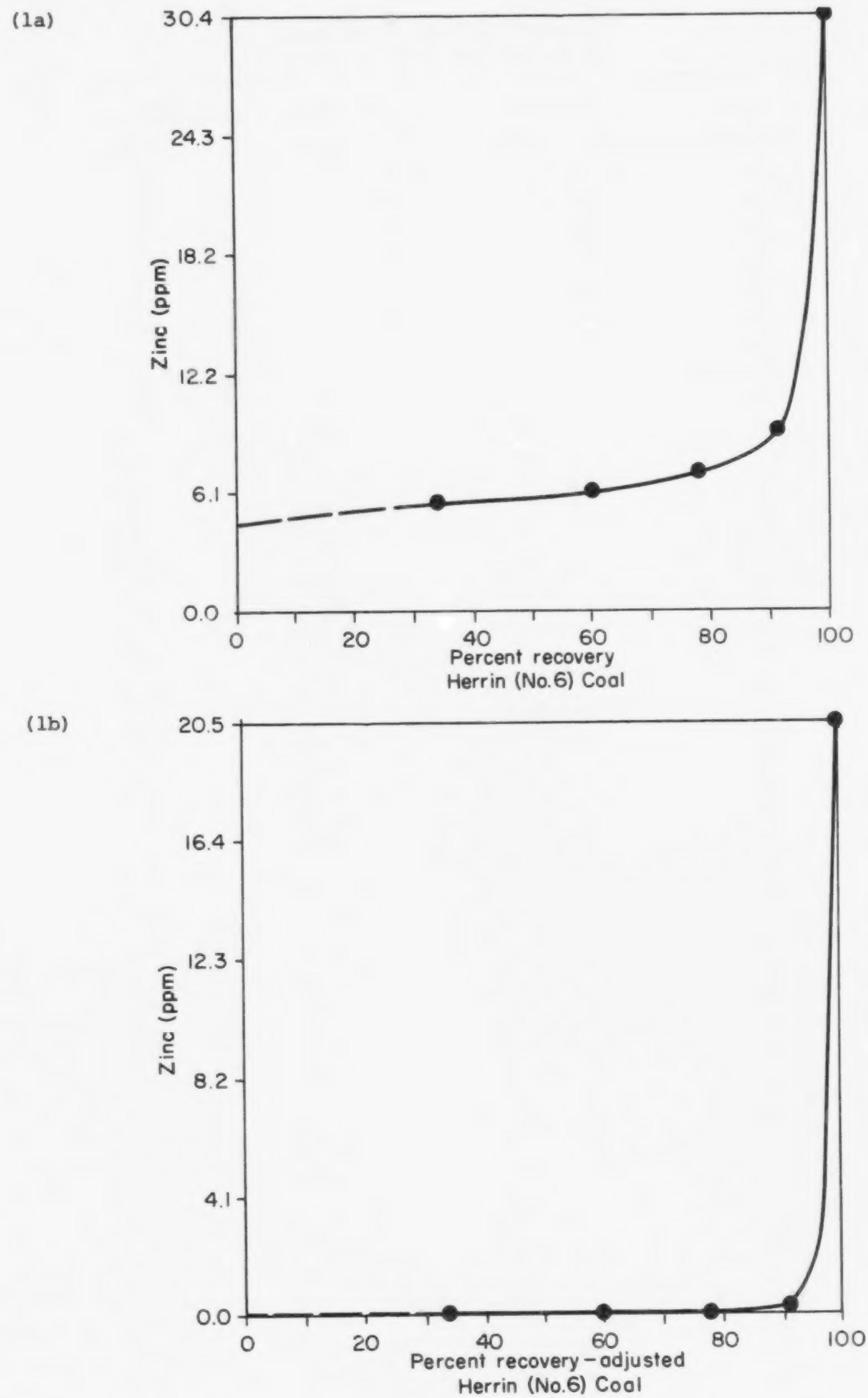
(1a)
30.4
24.3
18.2
12.2
6.1
0.0
Zinc (ppm)
0
20
40
60
80
100
Percent recovery
Herrin (No.6) Coal
(1b)
20.5
16.4
12.3
8.2
4.1
0.0
Zinc (ppm)
0
20
40
60
80
100
Percent recovery – adjusted
Herrin (No.6) Coal

Figure 1

TABLE 3

ELEMENTAL CONCENTRATIONS IN AN EASTERN COAL (C-18820)

Element	Raw Coal		F/S EXT		MMF	
	%	ppm	%	ppm	%	ppm
Al	1.41		0.0			69
Ca	.56		.11			34
Fe	.56		.34			72
K	.23		.0			<10
Si	2.51		.0			56
Ti	.12		.01			19
Mg	.06		.00			18
Na	.07		.00			.5
Organic S	.50		.60		.47	
Br		24		27		16
P		26		13.7		.1
V		22		.00		1.5
Mn		14		1.6		.5
Sn		.3		1.0		<.1
B		12		2.0		9.7
Cu		20		6.7		6.5
Co		7.5		7.9		6.5
Ni		12		12		5
Be		.88		.94		.11
Cr		20		3.5		6.3
Mo		4.6		1.7		<1.0
Sr		96		82		50
Pb		1.6		.6		LD
Zn		12		1.1		.3
Cd		<.1		.09		<.1
As		15		.29		<.5
Ga		4.2		1.1		.7
Se		5.8		1.1		1.0
U		1.0		.15		.2
Ba		180		118		33
Ce		31		7.5		.1
Hf		1.5		.19		.2
La		19		5.8		5
Lu		.12		.04		.05
Rb		<.1		0.0		<.1
Cs		2.0		.0		.2
Sc		3.3		.9		2.0
Sm		1.5		.76		.9
Tb		.4		.13		.27
Dy		2		.86		.9
I		2.6				1.4
Ta		.12		.05		.09
Yb		.6		.24		.06
Te		.3				<.1
Th		6.2		.53		1.1
W		.5		.43		.12
Eu		.47		.19		.2
Sb		4.6		.36		<.4
ISA			129 m^2/g			

TABLE 4

ELEMENTAL CONCENTRATIONS IN AN ILLINOIS NO. 6 COAL (C-18560)

Element	Raw Coal		F/S EXT		MMF	
	%	ppm	%	ppm	%	ppm
Al	1.40		0.0			41
Ca	.51		0.0			25
Fe	2.60		0.0			66
K	.13		.02			<1.0
Si	3.20		0.0			41
Ti	.06		.01			20
Mg	.06		0.0			21
Na	.04		.01			6
Organic S	1.87		2.36		1.81	
Br		13.4		24		3.3
P		50		0.0		<1.
V		36		34.5		3.5
Mn		62		0.0		.3
Sn		.4		0.0		<.1
B		200		38		6.6
Cu		13		2.3		2.1
Co		7.2		1.42		.36
Ni		24		5.5		<1.0
Be		1.4		.68		.03
Cr		20		21		6.8
Mo		11				.52
Sr		33		1.7		1.5
Pb		<1		.03		<1
Zn		57		.0		1
Cd		<.1		0.0		<.1
As		3.4		0.0		<.07
Ga		2.4		0.0		.73
Se		4.3		0.0		.26
U		1.9		5.3		.09
Ba		54		0.0		.2
Ce		25		0.0		.1
Hf		1.1		.05		.11
La		6.1		0.0		.72
Lu		1		.02		.03
Rb		23		0.0		<1.0
Cs		2.0		.01		.1
Sc		4.1		.57		.65
Sm		.86		.11		.41
Tb		.1				.1
Dy		1.2		.61		.5
I		1.2				<.8
Ta		.12		.03		.09
Yb		.84		.05		.23
Te		1.				<.1
Th		3.6		.33		1.0
W		.6				.06
Eu		.26		.05		.1
Sb		.5		.47		.09
ISA			173 m^2/g			

TABLE 5

ELEMENTAL CONCENTRATIONS IN A WESTERN COAL (C-19000)

	Raw Coal		F/S EXT		MMF	
Element	%	ppm	%	ppm	%	ppm
Al	1.40		0.0			87
Ca	.46		.64			20
Fe	.40		.27			65
K	.02		.00			<10
Si	1.40		0.0			87
Ti	.06		0.0			54
Mg	.07		.06			<20
Na	.17		.15			1.4
Organic S	.38		.38		.32	
Br		.9		1.2		1.0
P		120		91		<4
V		7.1		8.1		<5
Mn		8.3		.68		.4
Sn		<.2		0.0		<.2
B		37		37		5.3
Cu		4.7		2.0		<3
Co		.9		.5		.5
Ni		2.6		1.14		<1.5
Be		.39		.33		.03
Cr		3.4		.98		1.4
Mo		--		--		--
Sr		204		111		
Pb		LD		0.0		LD
Zn		3		4.7		<.5
Cd		<.1		.09		<.1
As		1.1		0.0		.2
Ga		2.3		0.0		.15
Se		1.6		.43		.6
U		.7		.13		.05
Ba		265		218		15
Ce		5.9		3.6		1.2
Hf		.64		.11		.20
La		6.0		1.36		1.3
Lu		.08		.03		.03
Rb		1.20		.34		<1.0
Cs		.11		.0		<.05
Sc		1.3		.50		.42
Sm		.80		.06		.03
Tb		.10		.03		.07
Dy		.65		.39		LD
I		.61				.3
Ta		.10		.01		.LD
Yb		.84		.05		.23
Te		.6				.2
Th		1.4		.00		0.6
W		1.2		.03		.LD
Eu		.15		.03		.05
Sb		.35		.09		.18
ISA			240 m^2/g			

estimated from adjusted washability curves (F/S EXT) and from analysis of the acid-washed mineral-matter-free (MMF) residues. Data are given for an eastern U.S. coal, the Illinois Herrin (No. 6) Coal and a western U.S. coal. Comparison of concentrations for F/S EXT and MMF shows that the majority are in close agreement. Exceptions include Ca, Fe, Be, and B in the eastern coal; Br, V, Be, U, and Sb in the No. 6 Coal; and Ca, Fe, Mg, Na, P, B, Be, Zn, and Ba in the western coal. It is likely that minor elements, i.e., major ash-forming elements such as Ca, Fe, Mg, and perhaps P, are for the most part inorganic but are incompletely removed during float/sink gravity separations. It is also likely that Na and Ba in the western coal; Br in the No. 6 Coal; B and Be in all three coals; and, perhaps, Se in somelllinois coals (not shown) are actually organic, as indicated by float/sink tests, but appear to be inorganic from the acid extraction evidence. That is, these elements may be loosely combined with the organic coal material and easily displaced from it by the acid treatment.

Although these data are still being combined with results from on-going pyrolysis and volatility studies, some preliminary conclusions can be drawn. Table 6 summarizes the means and correlations of the sulfur values determined for the mineral-free material and the values for organic sulfur obtained using the standard ASTM method (D2492) for analysis of raw coal. The means are in close agreement, which indicates that for the 25 coals analyzed in this study, the pyritic sulfur is quantitatively removed by the ASTM procedure.

The correlations between organic sulfur and the other elements determined in the coal samples are listed in Table 7. It is apparent that correlation with organic sulfur is not an indicator of the organic association of other elements. The data show that a significant correlation exists only if those elements were introduced into the coal-forming swamp at or near the same time as the organic sulfur or if the geochemical properties were sufficiently similar to cause deposition under similar conditions.

Table 8 shows the mean and standard deviation of the concentrations of 11 mineral-matter-free Illinois No. 6 Coal samples. Since some of the deviations equal or exceed the mean concentration, each coal must be evaluated separately in order to make predictions about organic associations and their effect on reactions during processing.

Finally, the data imply that most of the organically associated elements are rather weakly bound, having been deposited after the formation of the coal. Moreover, for the elements studied, no more than a very few parts per million can be considered an inherent part of the organic molecules. Therefore, it can be presumed that pollution or problems in coal combustion, liquefaction, or other processes will for the most part be associated with the inorganic matter in the coal. It is still possible, however, that enhanced volatility of an organically associated trace element could lead to its concentration in a process steam (gas or liquid effluent).

VOLATILE PRODUCTS FROM PYROLYSIS OF COAL

Volatilized constituents—organic and inorganic—from coal can be obtained by means of devolatilization of coal at low (≤250° C) and medium (250° C to 650° C) temperatures. Determination of these constituents and their relation to variations in the physical and chemical characteristics of different coals should yield information concerning the structure of coal as related to carbonization, gasification, and liquefaction. For this purpose, we have used several pyrolysis systems; Figure 2 shows the system as recently modified. Chars were prepared from 12 different coals by heating at temperatures ranging between 200° C and 900° C in 50° C-to-100° C steps. Analyses of the char and comparison with analysis of the whole coal yielded the following results:

1. Most coals exhibited similar behavior. For example, the Herrin (No. 6) Coal from Illinois, heated in steps to 700°C, showed a reduction of sulfur from 4.5 percent in the raw coal to 1.5 percent in the char, a 66 percent loss of sulfur on a whole-coal basis. Most of the sulfur was lost while the coal was heated between 300°C and 400°C.

TABLE 6

CONCENTRATIONS OF SULFUR IN 25 COAL SAMPLES

Type of coal	Number of samples	Mean percentage of organic sulfur in whole coal	Mean percentage of sulfur in MMF coal	Correlation coefficient
Eastern	5	.99	.95	1.00
Western	5	.43	.42	.96
Illinois No. 6	11	1.70	1.71	.98
Illinois No. 5 to No. 2	4	1.26	1.26	.99

NOTE: Values have been normalized to the same weight basis.

TABLE 7

CORRELATION BETWEEN ORGANIC SULFUR AND OTHER ELEMENTS

Element	Correlation coefficient	Element	Correlation coefficient	Element	Correlation coefficient
Al	-.16	B	.33	Ce	.10
Br	-.22	Cu	.24	Hf	-.14
Ca	.26	Co	-.35	Te	-.06
Fe	-.14	Ni	-.28	La	-.14
P	-.12	Be	-.18	Lu	-.35
K	.03	Cr	-.04	Eu	-.10
Si	-.21	Mo	.07	Cs	-.50
Ti	-.21	Sr	.12	Sc	-.27
V	-.16	Zn	.12	Sm	-.01
Mg	.14	As	-.13	Dy	-.45
Mn	.08	Ga	.44	I	-.21
Na	.01	U	.00	Th	.12
Sn	.06	Ba	.04	Sb	.07

TABLE 8

CONCENTRATIONS OF ELEMENTS IN 11 MMF ILLINOIS NO. 6 COALS

Element	Mean (ppm)	Standard Deviation	Element	Mean (ppm)	Standard Deviation
Al	60	14	Cu	3.5	1.6
Br	3.9	2.4	Co	.4	.2
Ca	42		Ni	5.7	5.4
Fe	63	28	Be	.04	.03
P	4.3	3.5	Cr	6.4	2.2
K	8.4	15	Mo	.8	.5
Si	56	20	Sr	4.2	3.3
Ti	30	15	Pb	1.8	3.2
V	7.1	4.4	Zn	1.7	1.3
Mg	28	9.8	Cd	.5	.5
Mn	.4	.2	As	.15	.07
Na	6.4	3.8	Ga	.6	.1
S	1.70	.48%	Se	.4	.2
Sn	.9	1.0	U	.2	.1
B	7.6	1.4			

Revised Pyrolysis Unit

Retort modification	June 24, 767-48
Furnace modification	June 28, 767-58
Collection modification	July 1, 767-71

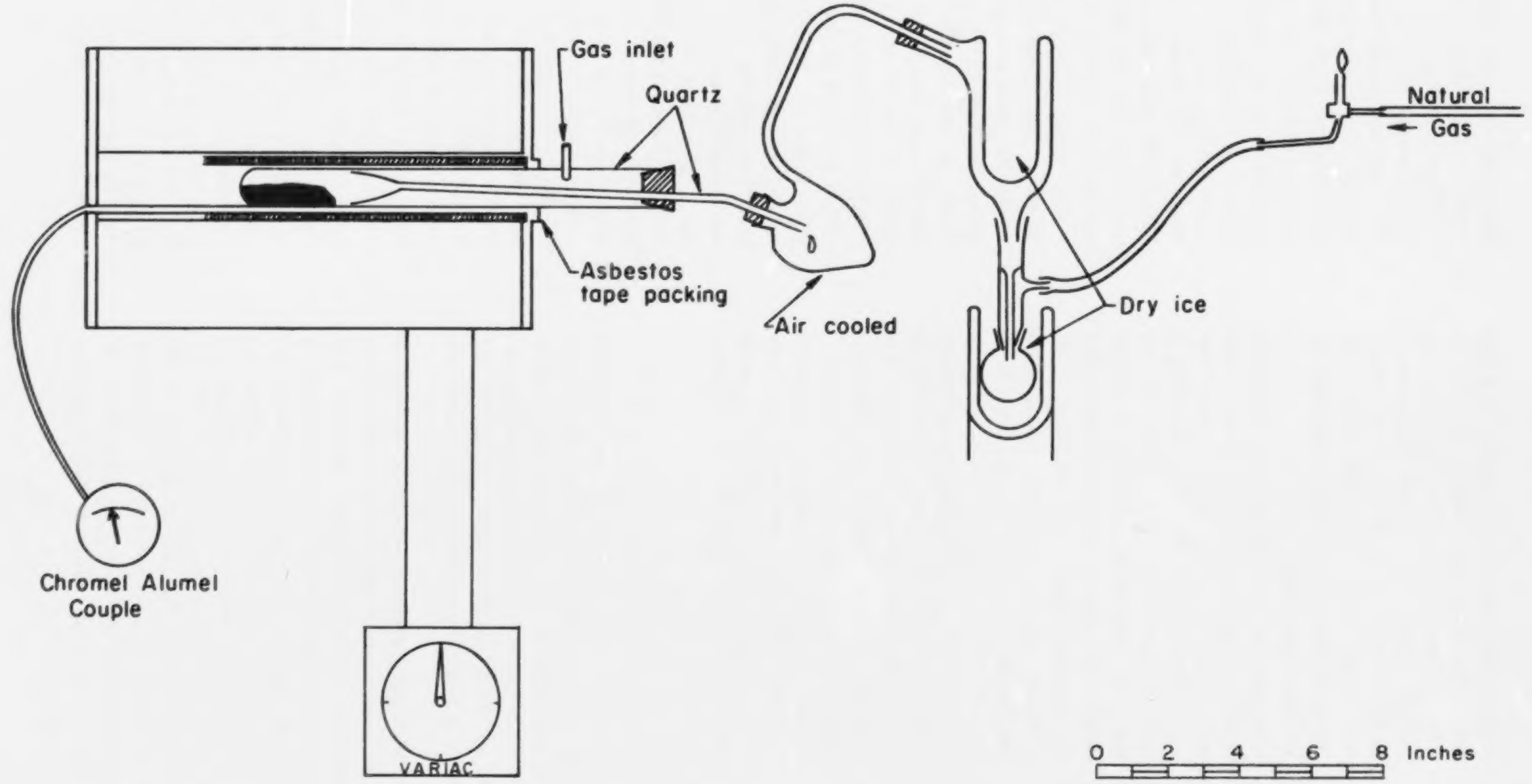
Gas inlet
Quartz
Asbestos tape packing
Air cooled
Dry ice
Natural Gas
Chromel Alumel Couple
VARIAC
0
2
4
6
8
Inches

Figure 2

2. Only a small amount of sulfur was lost while the char was heated to 700°C. The greatest rate of sulfur loss occurred over the same temperature range (300° C to 400° C) at which the coal char exhibited maximum Gieseler fluidity and minimum internal surface area (ISA).
3. The internal surface area of pyrolysis residues increased slightly when a coal was heated to about 300°C; ISA then exhibited a rapid decrease, reaching a minimum at 350° C to 400° C. As the coal was further heated to about 700° Cto 750° C, the ISA increased to approximately its original level. Heating above 750°C completely destroyed the original coal structure, and the ISA decreased. Thus, we may conclude that a coal changes continually as it is heated to higher temperatures in an inert atmosphere (nitrogen); the greatest change occurs as the coal passes through the 350°C-to-450°C range, at which it reaches maximum Gieseler fluidity, minimum surface area, greatest rate of sulfur loss, and release of the majority of volatile organics.

Because of the typical pyrolysis pattern observed, it has been concluded that for our studies the two most important temperatures for which volatility data need to be obtained are 450°C and 700°C. At 450°C reactivity is highest and most volatile products are released; at 700°C all volatile products are released but the coal structure (ISA) is still intact.

From iron-sulfide-phase equilibria studies, it is known that pyrite breaks down to pyrrhotite and sulfur at 743°C; however it appears that the pyrite contained in coal is converted to pyrrhotite at 450°C or lower in a nitrogen atmosphere. This is shown by X-ray diffraction analysis and scanning electron microscopy with energy-dispersive X-ray analysis of the mineral matter from the raw coals and of the chars produced by pyrolysis. Chemical analyses also indicate a greater loss of sulfur from the pyrite than organic sulfur at low temperatures, whereas the reverse is true at high temperatures (>450°C).

Determinations of trace elements for the whole coals and the resulting chars indicate that certain trace elements are lost through heating. The importance of assessing the levels and fate of trace elements volatilized during coal utilization is of concern from both economic and environmental standpoints. Highly volatile species may be lost from some conventional power plant emission control devices. The extent to which volatile species will create new hazards in coal conversion is unknown, and the effect of trace elements on conversion catalysts is still uncertain.

Six coals (Table 9) are currently being studied for trace-element volatility during pyrolysis under an inert gas (N_2) flow at 450°C (and later at 700°C) in order to simulate conditions in gasification and liquefaction. The percentage weight loss during pyrolysis is given in Table 10. Table 9 lists preliminary results of energy-dispersive X-ray fluorescence (XES) analyses of both the raw coals and the char residues. (Char values have been corrected for apparent concentrating effects from losses of volatile matter.) Indium, Sn, and Sb are volatilized and lost during pyrolysis, and Cd and Zn appear to be volatilized to a lesser degree. Support for this comes from atomic absorption analyses that indicate very small amounts of Cd are present in the trapped volatile fraction. Results based on instrumental neutron activation analysis (INAA) and wavelength-dispersive X-ray fluorescence (XRF) analysis indicate that As, Cl, Br, S, and Se are also lost in varying degrees while most other elements remain in the residue or are lost in amounts too small to be detected.

Direct analysis of the condensed volatiles from the pyrolysis system has proved to be difficult. The condensate is a tarlike material that is difficult to process without risk of contamination or loss. The quantities of trace elements are so low that lack of sensitivity is a problem in the determination of some elements by XRF methods. Such a material can also present a problem for INAA during irradiation in a nuclear reactor. Charcoal traps have been used to collect volatile species; however, with this

TABLE 9

PRELIMINARY XES DATA FOR PYROLYSIS OF SIX COALS

	C-18440		C-18571		C-18571-F		C-18847		C-18857		C-18185	
Element	Raw Coal	450°C	Raw Coal	450°C[a]	Raw Coal	450°C	Raw Coal	450°C	Raw Coal	450°C	Raw Coal	450°C
Cd	2.3	2.3	3.3	1.6	1.8	0.8	1.4	0.9	1.9	0.75	7.0	7.0
In	2.6	0.72	1.7	0.10	1.9	<0.1	2.0	<0.1	0.9	<0.1	0.8	<0.1
Sn	5.0	1.0	6.9	0.18	5.1	0.8	3.9	<0.1	2.2	.68	1.4	<0.1
Sb	5.6	2.0	5.2	0.07	5.8	1.0	5.0	<0.1	1.9	<0.1	3.3	<0.1
Te	1.3	4.4	0.7	0.56	0.9	0.3	1.5	1.4	0.8	1.1	0.5	1.8
I	3.9	8.5	2.7	1.4	1.4	0.8	3.2	3.0	1.8	1.4	2.5	2.8
Cs	9.2	26.9[b]	2.7	3.8	2.9	2.0	8.6	8.4	3.3	3.3	2.4	8.9[b]
Ba	337	1205	44	48.5	34.3	35.1	202	241	51	53.8	40	302
La	8.1	10.7	8.8		6.3	4.9	13.5	13.9	10.8	8.9	4.9	8.1
Ce	8.7	13.6	9.2		9.7	7.0	20.4	24.7	10.0	11.5	8.9	12.3
Zn	3.7	14.3	84.5	48.3	21.8	18.3	13.7	12.1	35.3	45.7	323	246
Br	2.3	2.8	7.2	10.0	10.1	7.1	2.7	1.9	9.1	5.7	4.4	5.0
Rb	4.9	6.4	12.1	11.1	10.3	8.6	14.0	10.9	12.3	10.0	9.2	9.4
Sr	241.	245.1	27.5	30.4	21.7	19.6	68.2	59.3	29.8	26.4	22.0	27.5

NOTE: All values expressed as μgr/gr.

[a] Average of two determinations

[b] Interference from Ba

TABLE 10

PERCENTAGE VOLATILE MATTER LOST DURING PYROLYSIS

Sample number	Seam and state	Percentage weight loss at 450°C
C-18857	No. 6 Illinois	32.2
C-18571	No. 6 Illinois	27.5
C-18571F	No. 6 Illinois	30.3
C-18440	Lignite North Dakota	33.9
C-18185	No. 5 Illinois	27.0
C-18847	Blue Creek Alaska	8.4

approach total entrapment is never certain, and the blank levels in the charcoal itself are often high and variable.

Consequently, work is progressing on a new laboratory trapping system of greater capacity. The system consists chiefly of a Parr reactor vessel; a water-jacketed, large-bore glass column packed with small pieces of plastic tubing to slow the gas stream and decrease the size of the bubbles; and the associated cold traps (−30°C and −80°C). The column through which the volatile gases are bubbled contains acetone and methanol to dissolve organics and dimethoxypropane to react with any water in the system to form acetone and methanol. A resin for adsorbing organics has been used, but no trace elements were detected in it. With this system, when high volatile "A" coals were pryolyzed, thick condensed tars have tended to collect and plug the gas inlet from the Parr reactor. In addition, some gas is still lost from the final cold trap when it is warmed to room temperature.

Attempts are being made to concentrate the volatile trace elements, if any, by burning the trapped organic material and then retrapping the released trace elements in a scrubber from which they can be precipitated. For some very volatile gases, it may be possible or even necessary to pass them directly from the pyrolysis unit to a combustion unit for trapping the trace elements. The volatile organic material given off contains innumerable compounds. Efforts are being made to identify those that contain sulfur by subjecting the sample of volatile organics to an acid-base-neutral compound separation. The three fractions thus obtained are then analyzed for the relative distribution of sulfur compounds by means of a gas liquid chromatograph equipped with a sulfur-specific flame-photometric detector. As expected, the major portion of the sulfur-containing compounds are in the neutral fraction. A few are in the basic fraction and fewer still in the acid fraction. An attempt is being made to identify the more clearly separated compounds by gas chromatography-mass spectroscopy.

Because the concentrations of some volatile trace elements are very low, a continuous-feed pyrolysis furnace is under construction. This unit will allow the pyrolysis of coal in sufficient amounts that concentrations of traces of additional volatile components can be detected and quantified.

BENEFICIATION OF CHAR

Three coal samples have undergone various pyrolytic treatments in a preliminary study to determine the effect of heat on the composition of the char produced and on subsequent beneficiation of the charred residues. The first of these, a Herrin (No. 6) Coal sample from Illinois, was heated under nitrogen in a Parr pressure reactor at 600°C for 48 hours, and the residue was separated into magnetic and nonmagnetic fractions (coal A, Table 11). The second sample, also from the Herrin (No. 6) Coal Member, was heated in the Parr pressure reactor at 650°C for 20 hours and again separated into magnetic and nonmagnetic fractions. (In addition, samples of this char are currently being subjected to Mossbauer, electron probe, and scanning electron microscope analyses to determine various mineral phases.)

Differences in the composition of the magnetic and nonmagnetic fractions of these two coals, as determined by X-ray fluorescence, are shown in Table 11. Percen-

TABLE 11

PERCENTAGE IRON CONCENTRATION IN MAGNETICALLY SEPARATED, HEATED COALS

	Coal A (%)	Coal B (%)	Coal C (%)
Original char	1.19	1.05	2.07
Nonmagnetic fraction	.61	.63	1.28
Magnetic fraction	1.28	1.50	3.06

TABLE 12

PYROLYTIC CONVERSION OF PYRITE TO PYRRHOTITE

Treatment (°C/hr)	Wt. Loss (%)	Total S (%)	Pyritic S (%)	SO_4 Sulfur (%)	N (%)	Ash (%)
175/6	0.5	4.27	1.82	.36	--	15.0
(Whole Coal)	--	4.37	1.86	.37	--	15.3
650/48	33.0	2.39	0.08	--	0.94	20.6
(Char)	--	3.04	0.10	--	1.19	--
650/48	33.0	1.03	0.04	0.01	1.00	12.6
(HCl-extracted Char)	--	1.21	0.05	0.01	1.18	--

NOTE: Upper values determined on analyzed basis; lower values on moisture-free and ash-free basis.

tage recoveries are not given and differences in elemental concentrations cannot be directly compared. Nevertheless, the results show a significant quantity of magnetic iron resulting from conversion of pyrite (nonmagnetic) topyrrhotite (magnetic) during heat treatment.

Table 12 shows the nearly total disappearance of pyritic sulfur in the two partially pyrolyzed coals (chars) and the reduction of total sulfur (from 3.04 to 1.21 percent) in the HCl-extracted char. Hydrochloric acid usually removes little sulfur from coal (only the sulfate sulfur and low concentrations of sulfides other than pyrite are soluble in HCl). In this case, however, pyritic sulfur has been extracted from the char by means of conversion to pyrrhotite, which is soluble in HCl. Future tests with the continuous-feed pyrolysis furnace should indicate the potential for producing cleaner chars by controlling parameters that will allow more efficient beneficiation of the products of pyrolysis systems.

MOSSBAUER SPECTROSCOPY STUDIES

Through a cooperative effort of Southern Illinois University with the Illinois State Geological Survey, a study of the kinds of iron in pyrolyzed coal residues has been made using Mossbauer spectroscopy. Samples of whole coal, coal pyrolyzed at 175°C for 6 hours, at 405°C for 48 hours, and at 550°C for 48 hours were supplied by the Survey to G. V. Smith, Professor of Chemistry at Southern Illinois University, for the Mossbauer study. In addition, a sample of unpyrolyzed vitrain and fusain were supplied. All samples were from the Herrin (No. 6) Coal Member.

Because of the high sensitivity and noninterference of Mossbauer effects, the presence of several iron species were demonstrated in whole coal and in its pyrolyzed residues. Differences in isomer shifts and quadrapole splitting between pure pyrite and pyrite in coal indicate that there may be an interaction between the pyrite and the organic coal matrix (Smith, 1977). Recent investigations by A. Volborth (1977) support this conclusion, which may well have been first postulated by G. Cady (1935). The association appears to break down when the coal is heated to temperatures even as low as 175°C. Any amorphous iron sulfide present (isomer shifts indicate this possibility) in the whole coal is converted to pyrite at low temperatures. Further, advances in instrumentation and data reduction techniques have made it possible to identify four Fe^{+2} species in heat-treated coal samples. Previously, two types of iron were recognized in whole coal samples.

For our samples, the total quantity of iron species in different coal lithotypes are about the same, but have different distributions. The single fusain sample had the least amount of Fe^{+2} when compared to the vitrain or whole coal sample used. Two types of pyrrhotite have been identified in the heat-treated samples. One is unstable and contains dissolved sulfur, which is apparently liberated as the temperature is increased. The heat treatment in an inert, atmosphere tends to produce little change in Fe^{+2} species. It has been observed, however, that when a coal has been evacuated for the determination of these Fe species, then subsequently reexposed to air, and finally reevacuated, the types of iron change dramatically. This phenomenon may result from the removal of protective gases from the pores in the coal; the significance of this event in relation to spontaneous combustion is being investigated further.

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TREATMENT OF PHENOLIC WASTES

Stanley L. Klemetson, Ph.D., P.E.
Associate Professor
Environmental Engineering Program
Engineering Research Center
Foothills Campus
Colorado State University
Fort Collins, Colorado 80523

Abstract

The treatment of phenolic compounds from coal gasification plants using ultrafiltration and hyperfiltration is presented. Dynamically formed hydrous zirconium (IV) oxide membranes on several types of supports were the focus of the investigation. The pH variations of 6.5 to 11, pressure variations of 250 to 1000 psig (1724 to 6895 kPa) and concentration variations of 1 to 400 mg/l were examined. Phenol reductions greater than 95 percent were obtained with several membranes, and flux rates were greater than 100 gpd/sq ft (4.08 cu m/day/sq m).

INTRODUCTION

The energy problems which have developed recently in the United States have made it desirable to examine new methods of utilizing the lignite coal that is present in abundant quantities in western North and South Dakota, Montana and Wyoming. One of the solutions to this problem is seen in the conversion of coal to a clean fuel by the use of a coal gasification process. By gasifying the coal, a synthetic natural gas can be produced which is basically free of the sulfur present in the coal and is cleaner to use. A primary concern is that the treatment and/or conversion process that generates the clean fuel does not itself become a major pollution source. While the potential pollutants can be expressed in any or all of the three possible states of air emissions, solid wastes, and liquid effluents, all of them ultimately contribute to the wastewater effluents of the plant and its site. If coal gasification plants are to be constructed, the pollutants which are generated during their operation must be dealt with if their environmental effects are to be minimized.

Various types of processes have been developed to produce synthetic natural gas. Since the Lurgi gasification process is currently being planned for several sites in western North Dakota, the wastewater effluent concentrations produced by the Lurgi process was used as a basis of this study. However, the results should be applicable to many of the other processes also.

The purpose of this study was to determine the feasibility of utilizing hyperfiltration (reverse osmosis) or ultrafiltration to reduce the phenolic concentrations in the wastewater effluents for a coal gasification plant. Dynamically formed hydrous zirconium (IV) oxide membranes were the focus of the investigation. The applicability of Selas ceramic, Millipore and Acropor wrapped stainless steel, and carbon membrane supports were studied in relationship to the effects of pH variation, pressure variation, and phenolic compound concentrations.

COAL GASIFICATION PROCESS

The Lurgi coal gasification plants planned for construction in the United States are being designed to produce 250 million standard cubic feet (7.0 M cu m/day) of medium to high Btu synthetic natural gas that will yield about 970 Btu/std cu ft (36.14 MJ/cu m). The average consumption of coal in these plants is about 1000 to 1500 tons per hour (252 to 378 kg/s), and the annual water usage is about 17,500 acre-ft (21.58 M cu m).[1]

The coal is gasified with oxygen and superheated steam in the Lurgi pressure gasification process. The gasifier vessel consists of zones in which various gasification reactions take place. The combustion of the coal produces methane in a three-stage reaction: preheating and carbonization, gasification or devolitilization, and partial combustion. The temperature ranges from about 1150 to 1400° F (621 to 760° C) and the pressure ranges from about 350 to 400 psig (2413 to 2758 kPa).[2]

Most of the potentially hazardous materials are produced in the gasifiers, but there are no direct liquid or gaseous emissions of these materials from the units. Coal ash is the only direct waste discharge from the gasifiers. The ash is generally water quenched to cool and to prevent the production of airborne dust. The quenching water is considered a minor wastewater stream. A simplified flow diagram for wastewater treatment in the coal gasification process is shown in Figure 1.

The crude gas leaving the gasifier has a temperature of 700° to 1100° F (371° to 593° C), depending upon the type of coal used, and is under a pressure of about 400 psig (2758 kPa). It contains the carbonization products such as tar, oil, naphtha, phenols, ammonia, and traces of coal ash and dust. The crude gas is quenched by direct contact with a circulating gas liquor in a scrubber-decanter tower. The gas liquor effluent is sent to the gas liquor separator for the removal of tars and oils.

Following the removal of some of the tars and oils from the gas liquor in the Tar-Gas Liquor Separation unit, the water effluents are further treated in the Phenosolvan unit for the removal of phenolic compounds by passing through a multistage countercurrent extractor using isopropyl ether as the organic solvent. The waste effluent of the phenol recovery unit is subjected to ammonia recovery by fractionation and condensation to produce anhydrous ammonia.

Following this initial processing, the wastewater is to be subjected to further purification systems, such as ultrafiltration and hyperfiltration. Ideally, a wastewater cleaning system should be designed so that the water can be reclaimed for use as either boiler feed water or cooling tower makeup water. The removed and concentrated contaminants would also require a final safe disposal.

In the coal gasification operation the major sources of wastewater are the scrubber-decanter which follows immediately after the gasifier, and the condenser following the shift converter. The quantity of wastewater which will be produced is approximately as follows: 3.3 mgd (12.49 k cu m/day) will be generated in the scrubber-decanter, 1.1 mgd (4.16 k cu m/day) by the condenser following the shift converter, and 0.8 mgd (3.08 k cu m/day) by the steam stripping of the scrubber-decanter water to remove ammonia. Thus, approximately 5.3 mgd (19.68 k cu m/day) is produced which will require treatment. There are also some other relatively minor sources.[3]

WASTEWATER CHARACTERISTICS

During the gasification process, the byproducts from the gasifiers are condensed along with the water. Oil and tar are separated from the aqueous phase of the gas liquor, and the latter eventually mixes with the phenol containing wastewaters from other parts of the plant. This effluent was considered "raw wastewater." Usually the raw wastewater goes through a filtration process, extraction of phenols, and the removal of ammonia. After this initial amount of treatment the effluent

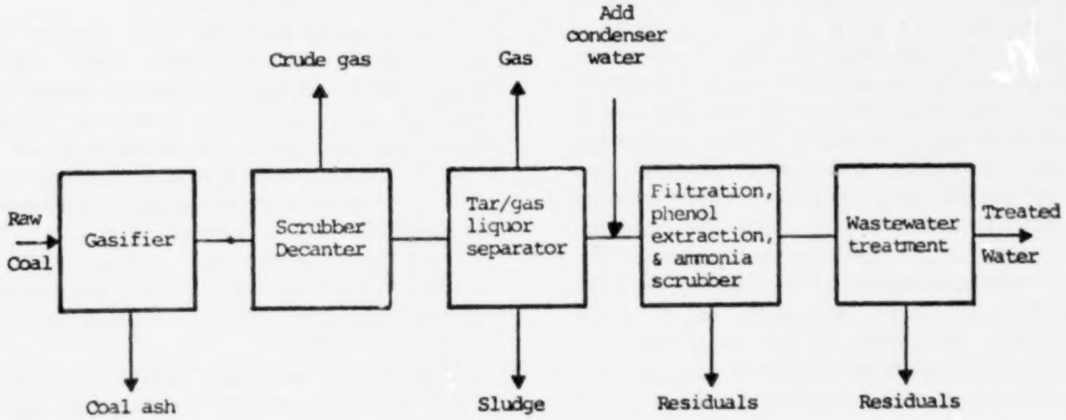

Figure 1. Flow diagram for wastewater treatment system.

"processed wastewater." When the processed wastewater had been subjected to biological treatment, it was designated as "bio-treated wastewater."

The concentration of phenolic compounds in the wastewater effluents of the Lurgi process plant of the South African Coal, Oil, and Gas Corp. Ltd., Sasolburg, South Africa (Sasol) has been reported by De W. Erasmus.[4] A typical analysis for their processed wastewater is 1-10 mg/l for monohydric phenols (Koppeschaar method), and 170 to 240 mg/l for the total phenols. Experience at Sasol has shown that the ratio of multihydric to monohydric phenols is reasonably constant and on the order of 20 to 40:1.

Sources from the Lurgi gasification plant of Stein Kollingas A. C. at Dorsten, German Federal Republic, reported 12-56 mg/l of monohydric phenols and 228-390 mg/l of total phenols. Cooke and Graham[5] also reported that in the processed wastewater from a Lurgi plant, the monohydric phenols (mostly phenol) comprise a minor part of the total phenols, while catechol and resorcinol (dihydric) account for the most of the fraction.

Barker and Hollingsworth[6] reported that catechol, resorcinol, hydroquinone, and their methylated derivatives in ammonical liquor are quite similar in composition to Lurgi processed effluent. They also indicated that trihydric species of phenol were also present in the same effluent.

Chambers et al.[7] made a study of the biochemical degradation of various phenol derivatives by bacteria adapted for the decomposition of phenol. They found that dihydric phenols may be oxidized quite easily along with monohydric phenols, while trihydric phenols were plainly resistant to decomposition by these bacteria.

Samples of the raw and processed wastewaters for the gasification of North Dakota lignite coal were obtained from Sasol by North Dakota State University. The analysis of the samples were conducted by Fleeker[8] and the biological oxidation of the processed water was performed by Bromel.[9] The rate of degradation of phenols was determined for a mixture of four Arthrobacter species and one Pseudomonas specie. From an initial total phenol concentration of 322 mg/l the bacteria reduced the concentration to 69 mg/l in a twenty-four hour period, and to 50 mg/l in five days; approximately 80 percent reduction. The monohydric phenols were reduced an equivalent amount from 69 mg/l to 8.3 mg/l. Bromel also reported that the residual recalcitrant compounds, possibly the multihydric phenols, may represent a potential problem in the effluents that will require chemical or physical treatment beyond biological treatment.

Although most of the phenols will be reduced in concentration to relatively low levels by the biological treatment methods, there will still be a large enough concentration remaining in the processed wastewater to potentially cause extensive contamination of the groundwater system. The standard recommended for phenol concentrations in potable water is 0.001 mg/l.[10] Phenols are highly toxic and increasingly so when chlorine is added to the water as most water treatment facilities do.[11] Concentrations of phenol on the order of 10 to 100 μg/l can cause undesirable tastes and odors. Trace amounts approaching 1 μg/l can impart an objectionable taste to a water following marginal chlorination.[12]

HYPERFILTRATION AND ULTRAFILTRATION

Osmosis and Reverse Osmosis

Osmosis is defined as the spontaneous transport of a solvent from a dilute solution to a concentrated solution across an ideal semipermeable membrane. The membrane acts as a barrier to the flow of molecular or ionic species and permits a high permeability for the solvent, water, and a low permeability for the other species. If the pressure is increased above the osmotic pressure on the concentrated solution side, the solvent flow is reversed. Pure solvent will then pass from the solution into the solvent. This phenomenon is referred to as reverse osmosis.

Hyperfiltration and Ultrafiltration

Filtration separation can be classified into four families: (1) screening - removal of large particles; (2) filtration - removal of smaller particles; (3) ultrafiltration - removal of colloidal particles; and (4) hyperfiltration - removal of low-molecular-weight dissolved materials. The boundaries between the various classes are not precisely defined.

Much of the ultrafiltration mechanism can be interpreted in terms of selective sieving of particles through a matrix of pores of suitable dimensions. The removal of low molecular weight molecules cannot be reduced to geometric terms because there is no significant difference in the size of water molecules and the size of many inorganic ions. Therefore, ultrafiltration is unsuitable in this size range. The hyperfiltration membrane thus affects the thermodynamic and transport properties of solutes and solvents by forces, i.e., Van der Waals or Coulombic. These do not depend primarily on the difference in size of the ions and molecules to be separated. Hyperfiltration is commonly referred to as reverse osmosis, since there are substantial differences in osmotic pressure between feeds and filtrates which must be exceeded when appreciable differences of weight concentration of low-molecular-weight solutes exists.

Ultrafiltration and hyperfiltration differ primarily because ultrafiltration is not impeded by osmotic pressure and is effective at low pressure differentials of 5 to 100 psig (34.5 to 689 kPa). The osmotic pressure plays a larger role as the molecular size decreases. The term "hyperfiltration" is also applicable to the separation of solutes with different permeation rates when the solution is forced through a membrane under pressure. The term is descriptive even if the solute to be removed is a trace concentration and does not contribute significantly to the osmotic pressure.[13]

Membranes

Hyperfiltration membranes can be classified into two basic categories: neutral and ion-exchange. Both approaches to membrane development were recognized at about the same time. But because of the favorable properties of a specific neutral type (the Loeb-Sourirajan cellulose acetate membrane[13]); the cellulose acetate membranes have received most of the attention. Both flux and rejection of cellulose acetate membranes were high compared to those observed with available ion-exchange membranes which were designed for low water permeability. Since flux is inversely proportional to thickness, a much thinner ion-exchange layer was needed to realize the potential flux advantages that a more loosely structured membrane filtering by ion exclusion could provide.

Several membrane configurations have been proposed and tested. Many configurations involve preformed or precast membranes which require equipment disassembly for installation and removal. The type of membrane of concern in this paper is dynamically formed and does not require disassembly for formation or removal. Dynamically formed membranes are formed at the interface of a solution and a porous body from materials added to the solution as it circulates under pressure past the porous body.[13] Only limited success of dynamically formed membranes from neutral additives has been reported.[15]

The dynamic formation technique has made possible the development of thin dynamically formed ion-exchange membranes. Thus, the high permeability of 1400 gpd/sq ft (57.12 cu m/day/sq m) with a rejection of about 50 percent that was expected of thin ion-exchange membranes can be attained, particularly if they are formed with fast circulation of feed past the porous supports or with high turbulence.[13,16,17]

Several types of polyelectrolyte additives were found to form this type of ion-exchange membrane, e.g., synthetic organic polyelectrolytes,[18,19] hydrous oxides,[20,21] and natural polyelectrolytes such as humic acid.[19] Membrane formation is not limited to soluble polyelectrolytes or colloidal dispersions. It was found that particulates such as clays could form membranes as well.[19,22]

In many cases salt removal is unnecessary, or even undesirable; consequently, a membrane which passes salt while concentrating other matter is preferred. Several dynamically formed ultrafiltration membranes using hydrous oxide and polyvinyl priolidone have been tested successfully.[23]

Many materials can be used as porous supports: filter sheets such as Millipore and Acrepor, porous metal, carbon tubes[19]; ceramic tubes[24]; and woven fabric.[25] For most types of ion-exchange membrane additives, the favorable pore size range lies between 0.1 and 1.0 microns.[13]

Some attractive features of many dynamically formed membranes include the ability to operate at elevated temperatures, allowing treatment of waste streams at process temperatures and recycle of the hot water. A negative aspect is a deterioration of performance from polyvalent counter ions in feed.[13] Membrane regeneration can be relatively simple and inexpensive, since the deposit of active membrane can be removed by flushing and reformed by pumping through a dilute suspension of active material. Also, the higher fluxes that can frequently be obtained allow the use of tubular geometries without undue sacrifice in production rate per unit volume.[28]

EXPERIMENTAL

Procedure

The test equipment was so constructed that a pressurized solution, containing selected additives during membrane formation and consisting of the effluent to be studied during membrane evaluation, could be circulated past porous supports under controlled conditions of temperature, pressure, pH, and circulation velocity.

The feed solutions, a synthetic representation of the coal gasification wastewater, were prepared with reagent-grade phenol, resorcinol, o-cresol, and catechol. Tests included feed concentration variations of 1 to 100 mg/l for solutions prepared with all four phenolic compounds. Tests conducted solely with phenol ranged in feed concentration from 1 to 400 mg/l. Reagent grade pentachlorophenol was also used as a feed solution at 10 mg/l.

The range of pH used in testing varied from test to test between 5 and 12, and similarly the pressure ranged from 200 to 1000 psig (1379 to 6895 kPa). The temperature variation examined was 25° to 55° C for the ultrafiltration tests, and the hyperfiltration tests were conducted at a constant 30° C. Ultrafiltration tests were maintained at a constant pressure of 200 psig (1379 kPa). A constant flow rate past the membranes of 15 ft/sec (4.57 m/s) was maintained for all tests. Concentrated nitric acid and one normal sodium hydroxide were used to adjust the pH of the feed solution.

In each experimental run, the observed rejection was determined on the basis of salt conductivity and solute concentrations, and the results were expressed as a percent rejection. The flux or permeation rate through the membranes was determined and expressed as gpd/sq ft of membrane surface. While most of the test runs were conducted at specific operating conditions and were for a limited duration, several apparent optimum operating conditions were chosen for some extended-run experiments designed to measure the deterioration of the membrane with operating time.

Equipment

All of the experimental work conducted on this project was done at the Oak Ridge National Laboratory in Oak Ridge, Tennessee. The hyperfiltration loop at that facility is shown photographically and schematically in Figure 2. Feed solution was drawn from feed tank G by the Milroyal type C triplex pump C (5 gpm (0.32 l/s) at 1500 psig (10.34 MPa) capacity) and forced under pressure into the circulation pump B, a 100-A Westinghouse centrifugal pump which was rated at 100 gpm (6.31 l/s) at 100 psig (689 kPa) head. This pump circulated the feed solution through the loop and past the membrane supports, which were placed in test sections A and A' (only one test section is shown in the photograph). The test sections were designed to direct the feed solution through the annular region between a tubular porous support, upon which the membrane was formed, and the wall of a stainless steel cylindrical pressure jacket (Figure 3). Flow velocities past the membrane surfaces, typically 10 to 35 ft/sec (3.05 to 10.67 m/s), were monitored by meters at D, the temperature of the feed was controlled by the tube-in-tube heat exchanger E, and the pressure was regulated by a pneumatically controlled valve in the letdown line which returned the feed to the tank at atmospheric pressure. The product which permeated the membranes was monitored as to flux and composition, and was returned to the feed container to maintain constant feed composition.

All of the materials used in the loop were corrosion-resistant to minimize interference of corrosion products with the formation of the

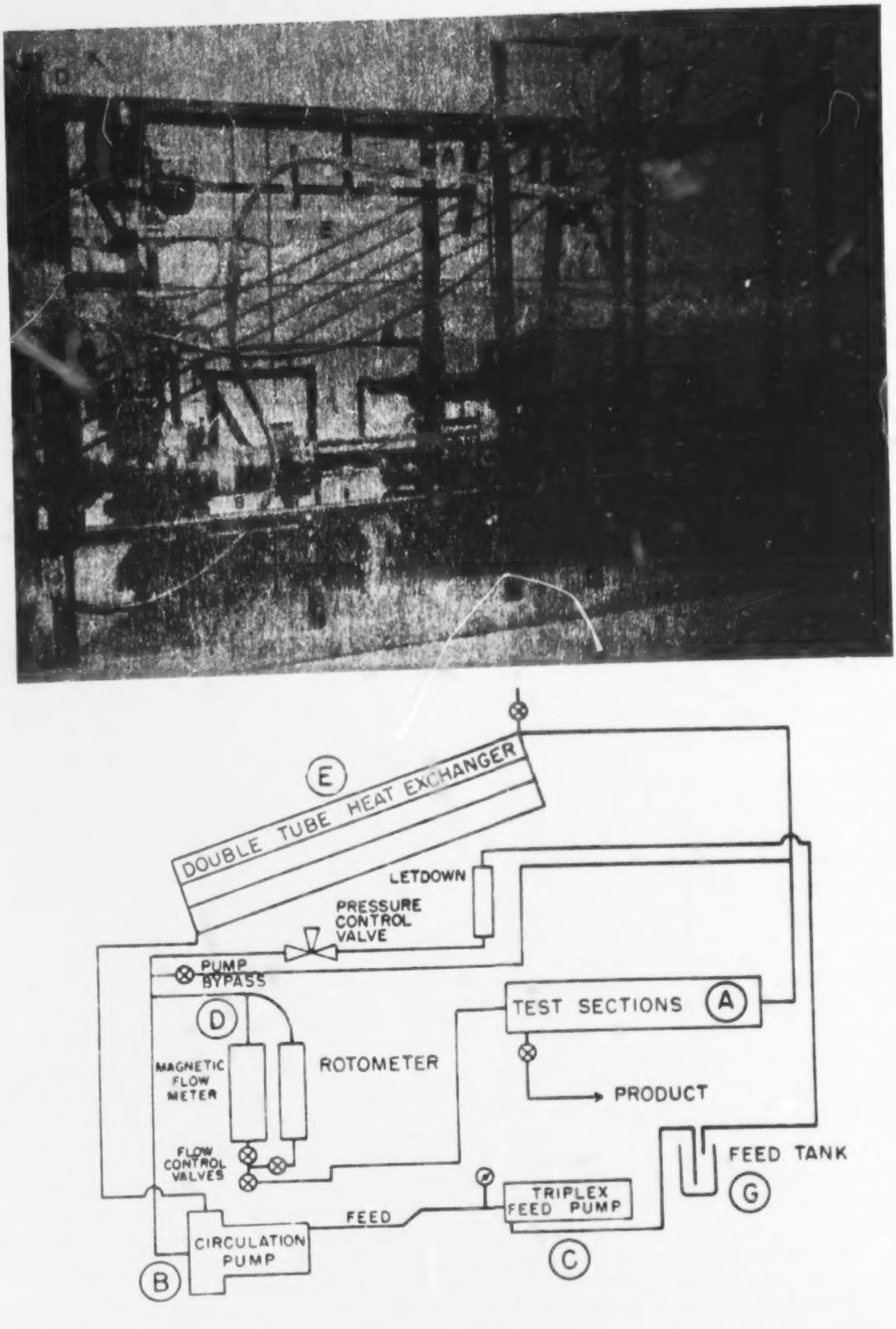
E
DOUBLE TUBE HEAT EXCHANGER
LETDOWN
PRESSURE CONTROL VALVE
PUMP BYPASS
D
MAGNETIC FLOW METER
ROTOMETER
TEST SECTIONS
A
PRODUCT
FLOW CONTROL VALVES
FEED TANK
G
TRIPLEX FEED PUMP
FEED
CIRCULATION PUMP
B
C

Figure 2. Hyperfiltration Loop.

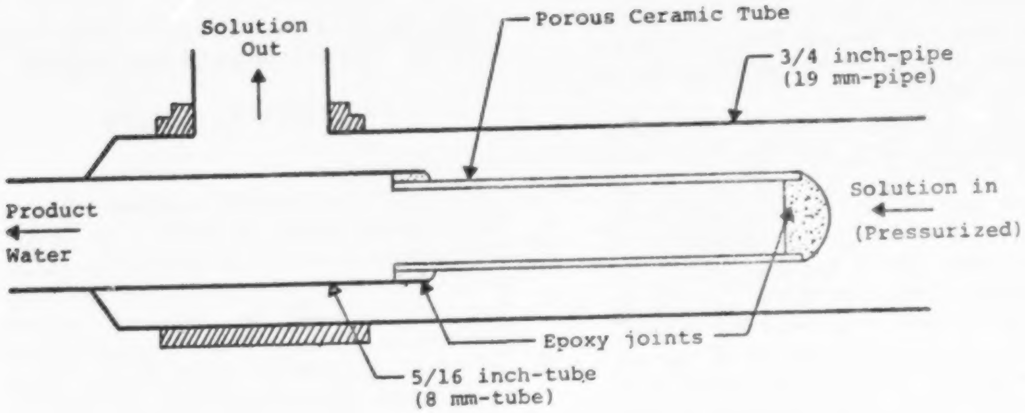
Solution Out
Porous Ceramic Tube
3/4 inch-pipe (19 mm-pipe)
Product Water
Solution in (Pressurized)
Epoxy joints
5/16 inch-tube (8 mm-tube)

Figure 3. Mounting of typical test section with ceramic tube support.

membranes. The loop was designed to eliminate stagnant side volumes in which material might collect and contaminate subsequent experiments. The ultrafiltration loop consisted of a configuration similar to the hyperfiltration loop.

Porous Supports

Several different porous support materials were used. Acropor AN sheets, a copolymer of polyvinyl chloride and polyacrylonitrile on a nylon substrate made by Gelman Instrument Company, Ann Arbor, Michigan; and membrane filter sheets made from mixed esters of cellulose by Millipore Filter Company, Bedford, Massachusetts, were wrapped around 5/8 inch (15.9 mm) porous stainless steel tubes (pore size - 5 μm). Porous carbon tubes, Union Carbide Corporation's 563-6C (6.0 mm I.D., 10.25 mm O.D., undetermined pore size) and a porous ceramic tube, the Selas Ceramic filter element made by Selas Flotronics Corporation, Spring House, Pennsylvania, were also used.

Membrane Formation

The membranes were formed in carefully cleaned equipment to eliminate the possible interference of contaminants. Between each test run, the loop was cleaned by using a one molar sodium hydroxide wash, followed by a one molar nitric acid wash, and then distilled water.

The porous supports were inserted into the test sections. A solution of 0.04 molar sodium nitrate and 0.0001 molar zirconium oxide nitrate ($ZrO(NO_3)_2$, adjusted to a pH of 4, was circulated through the loop. As the hydrous oxide was deposited on the supports, the pressure increased. Once full pressure (900 psig (6205 kPa) to 1000 psig (6894 kPa)) was achieved, the salt rejection was monitored until it reached a value greater than 30 percent, which usually took an hour or more. Then a solution containing 50 mg/l of polyacrylic acid (PAA, Acrysol A-3 by Rohm and Haas) was added to the loop, and the pH was adjusted to 2. This solution was circulated past the membrane for about 30 minutes. After this time, the pH was raised to about 3, maintained there for another 30 minutes, and again raised a unit or so. This stepwise increase in pH was repeated until the solution was near neutral. At that time, the formation of the membrane was considered complete.

Two variations of the formation procedure included omitting the polyacrylic acid layer and substituting a silicate layer for the polyacrylic acid by adding 50 mg/l of sodium metasilicate (Na_2SiO_3).

Analytical Procedures

Routine monitoring of salt (observed) rejection was by conductivity with a conductance bridge and a cell with a precalibrated cell constant. Supplemental chloride analysis with a Buchler-Corlove chloridometer was performed in which the chloride ion concentration was determined by coulometric-amperometric titration with silver ion. This was done to check the mechanical integrity of the membrane for the absence of defects.

Phenol and phenolic compound combination concentrations were monitored by two methods. For test runs in which the feed concentration was greater than 10 mg/l phenol, the phenol concentration was determined by carbon analysis with a Beckman Model 915 Total Organic Carbon Analyzer. In this apparatus, the solution sample was injected into a high temperature (950° C) catalytic combustion chamber where the total carbon in the sample is oxidized in pure oxygen carbon dioxide which is analyzed by a Beckman Model IR-215A nondispersive infrared analyzer. Inorganic carbon was determined in a similar manner by injecting a sample into a 150° C combustion chamber and analyzing the carbon dioxide produced. The total organic carbon (TOC) was obtained from the difference between the total carbon and the inorganic carbon. Most of the feed solutions and many product solutions contained insignificant amounts of inorganic carbon. The analysis of total carbon was therefore essentially total organic carbon.

For a test run or a series of test runs in which the feed concentration of phenol was less than 10 mg/l, the Direct Photometric Method was used.[12] The principle of the method involved the reaction of phenol with 4-amino antripyrine at a pH of 10.0 ± 0.2 in the presence of potassium ferricyanide. The absorption of the prepared samples was measured on a Bausch and Lomb Spectronic 20 spectrophotometer at a wavelength of 510 nm. A standard calibration curve for phenol was prepared.

The color of the product and feed streams was determined with a Bausch and Lomb Spectronic 20 spectrophotometer at a wavelength of 465 nm and compared against platinum-cobalt standards.[12]

Pentachlorophenol concentrations were determined with a Cary Recording Spectrophotometer, Model 11 MS. The visible absorption spectra were scanned upward from 3000 angstroms to determine the exact wavelength for maximum absorption. This was found to be 3200 angstroms. All spectral measurements were made in a 10-cm silica glass cell. A calibration curve was prepared.

EXPERIMENTAL RESULTS

Hyperfiltration

The first hyperfiltration experiment utilized the zirconium oxide-polyacrylic acid (Zr(IV)-PAA) membrane with a feed solution composed of 100 mg/l each of phenol, catechol, resorcinol, and o-cresol. Six membrane support materials were tested. Three of these support materials, 6C carbon tube, 0.27-μ Selas ceramic tube, and 0.47-μ Acropor sheet on stainless steel tube, were used for the data presented in Figure 4. The tests were conducted at 25° C.

The results in the first three columns of Figure 4 indicate that the type of membrane support material has little effect on the performance of the dynamic membrane. The data are presented to show the effects of both pressure and pH on the operation of the membrane. The production of product water or flux rate is significantly increased by the increase of pressure, but the variation of pH has little effect on the flux rate.

The solute rejection rate increases from about 45 percent at a pH of 6.5 to about 80 percent at a pH of 10. It was expected that a pH of about 9.5 to 10 would produce the most significant reduction in the phenolic compounds because the phenolic compounds are sufficiently ionized at this pH to react favorably with the ion exchange properties of the membrane.

The salt rejection produced the opposite results by the rejection rate from about 92 percent to 85 percent as the pH is raised from pH 6.5 to 10. The maximum rejection of salt is best achieved near neutral pH. This characteristic is quite beneficial where the desire is to reduce the phenolic concentration without trying to remove all of the salt in the wastewaters.

The fourth column of Figure 4 presents data on the effect of different concentrations of the solute on the performance of the membrane. The Acropor membrane support produces a better flux rate than the other support materials, however, the variations in the con-

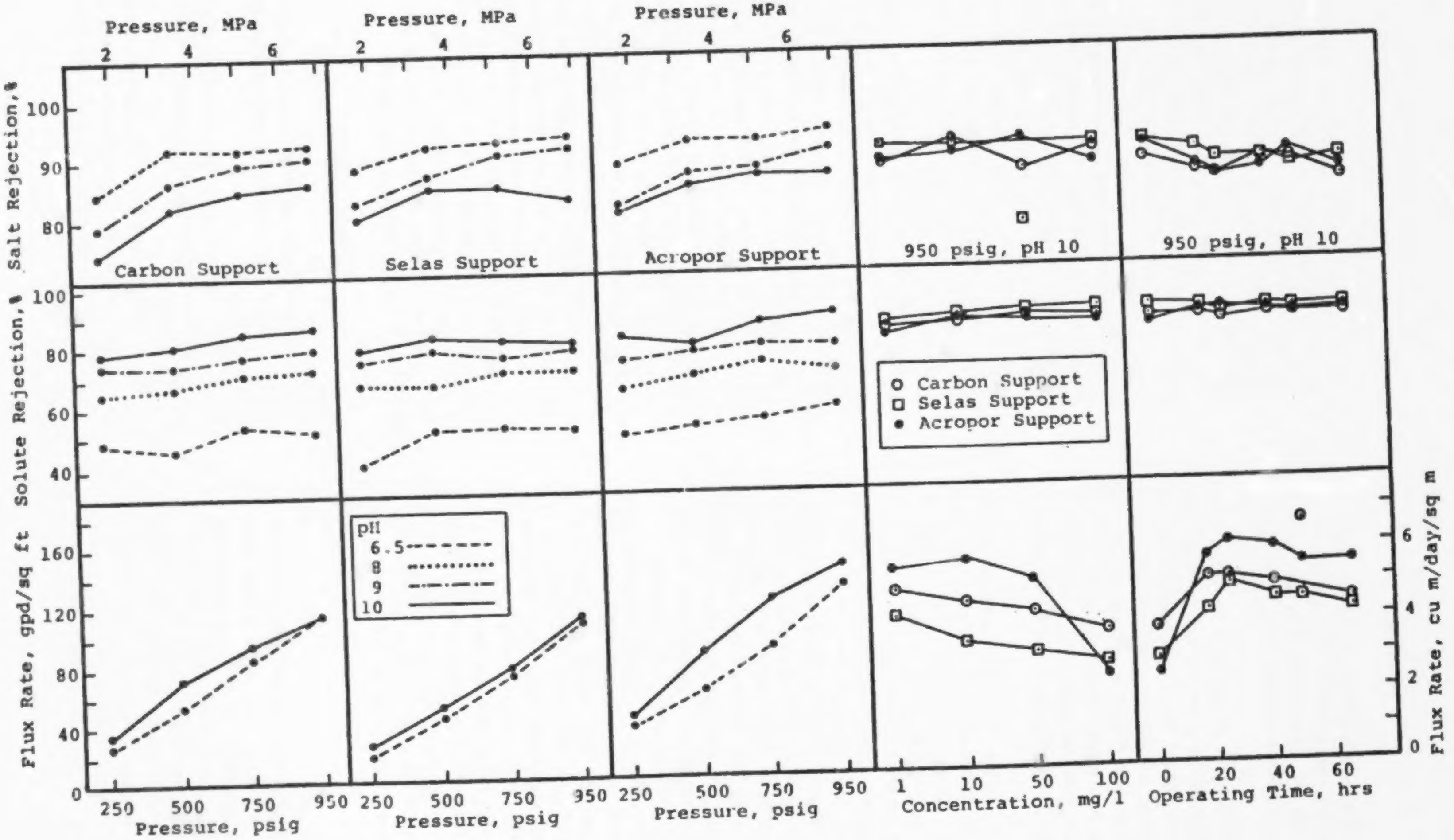

Figure 4. Hyperfiltration of Phenolic compounds (100 mg/l).

centration have little effect on the flux rate. The maximum flux rate is about 140 gpd/sq ft (5.7 cu m/day/sq m). The solute rejection and salt rejections remained constant at about 90 percent.

The final column of Figure 4 provides information about the long term effects of treatment on the operation of the membranes. The flux rate increased initially and then stabilized at about 150 gpd/sq ft (6.1 cu m/day/sq m). The solute rejection rates remained constant over the operating interval at about 90 percent. Salt rejection dropped slightly from 90 to 85 percent.

The next series of tests examined the suitability of zirconium oxide-polyacrylic acid (Zr(IV)-PAA), zirconium oxide-sodium silicate (Zr(IV)-Si), and zirconium (Zr(IV)) alone as membranes for the hyperfiltration of 10 mg/l of pentachlorophenol feed solution. The results are presented in Figure 5.

The first column of Figure 5 indicates that pH does have a significant effect on the flux rate of pentachlorophenol. While the zirconium membrane produced the highest flux rates, the solute rejection and salt rejection was far below the other membranes. The rejection of pentachlorophenol approaches 100 percent.

The second column of Figure 5 shows that the flux rate is virtually unchanged as pH increases, however, the solute rejection rate does increase with pH. The third column of Figure 5 indicates that flux rate rises with pressure. While the zirconium-silicate membrane produces the highest flux rate, the zirconium-polyacrylic acid provides the highest solute rejection at about 80 percent. The final column of Figure 5 again indicates that the membranes are stable for extended periods of time.

Ultrafiltration

Similar experimental parameters were examined under ultrafiltration. With a feed solution of 100 mg/l each of phenol, resorcinol, o-cresol, and catechol, tests were performed on three types of membranes on Selas ceramic supports: zirconium oxide (Zr(IV)), zirconium oxide-sodium silicate (Zr(IV)-Si), and silicate (Si). Figure 6 depicts a pH scan with the expected rejection increase at the higher pH. There is very little difference between the solute rejection rate for each type of membrane as the pH is increased. The data would indicate that it is the ionic state of the solute rather than the membrane that is the controlling factor in the rejection rate. The 75 percent solute rejection is below the 80 percent indicated on Figure 5 at a pressure of 950 psif (6.5 MPa).

As shown in column two of Figure 6, temperature of the feed water has a significant effect on the flux rate for some membranes. The flux for the zirconium oxide membrane increased from 60 gpd/sq ft (2.45 cu m/day/sq m) at 25° C to 160 gpd/sq ft (6.53 cu m/day/sq m) at 55° C. However, the salt and solute rejections appeared to be unaffected by the temperature changes.

Operating the filtration process for extended periods of time indicated a slight reduction of flux rate with time initially, followed by a long period of stable flow. The solute and salt rejections were unaffected by the operating time.

The sensitivity of the operation to variations in concentration was evaluated. Over a range of 1 mg/l to 400 mg/l of phenol, not significant variations in the data were noted.

A final test of the membranes, as shown in column five of Figure 6, was a pH scan from 6.5 to 12. Destruction or deterioration of the membranes was expected at the high pH values. The flux rate declined slightly as the pH was increased. The solute rejection increased significantly as the pH was increased above 8, but started to fall beyond pH 11. The salt rejection rate was the greatest at about a pH of 9, and fell down in both directions. In general the zirconium membrane outperformed the silicate membrane for the solute being tested.

CONCLUSIONS

The points of most general importance which have emerged from the foregoing studies are, briefly, as follows:

1. The carbon support tube produced slightly better rejection rates, but lower flux rates.
2. Increasing the pH of the feed increased the solute rejection rate, decreased the salt rejection rate, and had little effect on the flux rate.

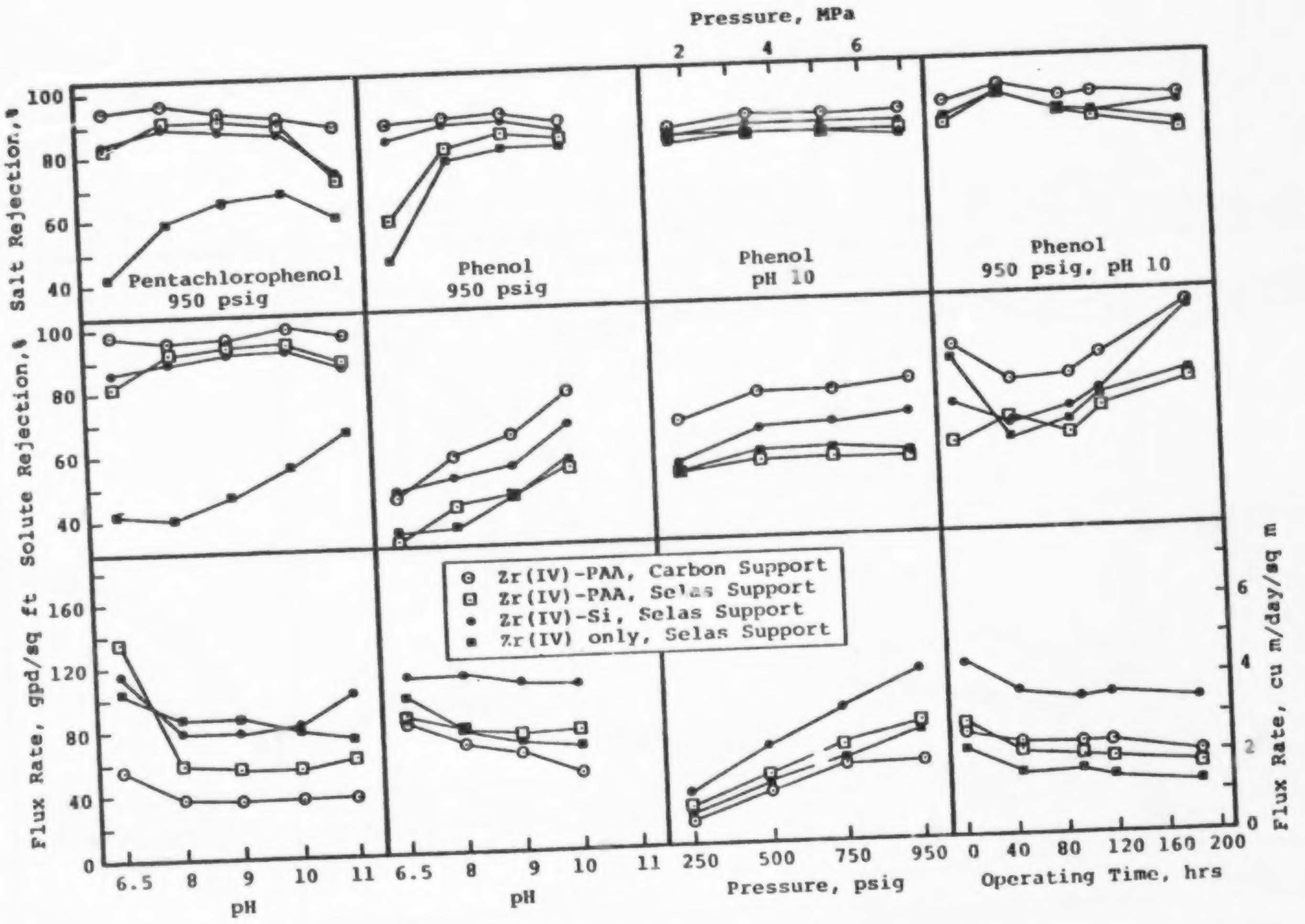

Figure 5. Hyperfiltration of pentachlorophenol and phenol (10 mg/l).

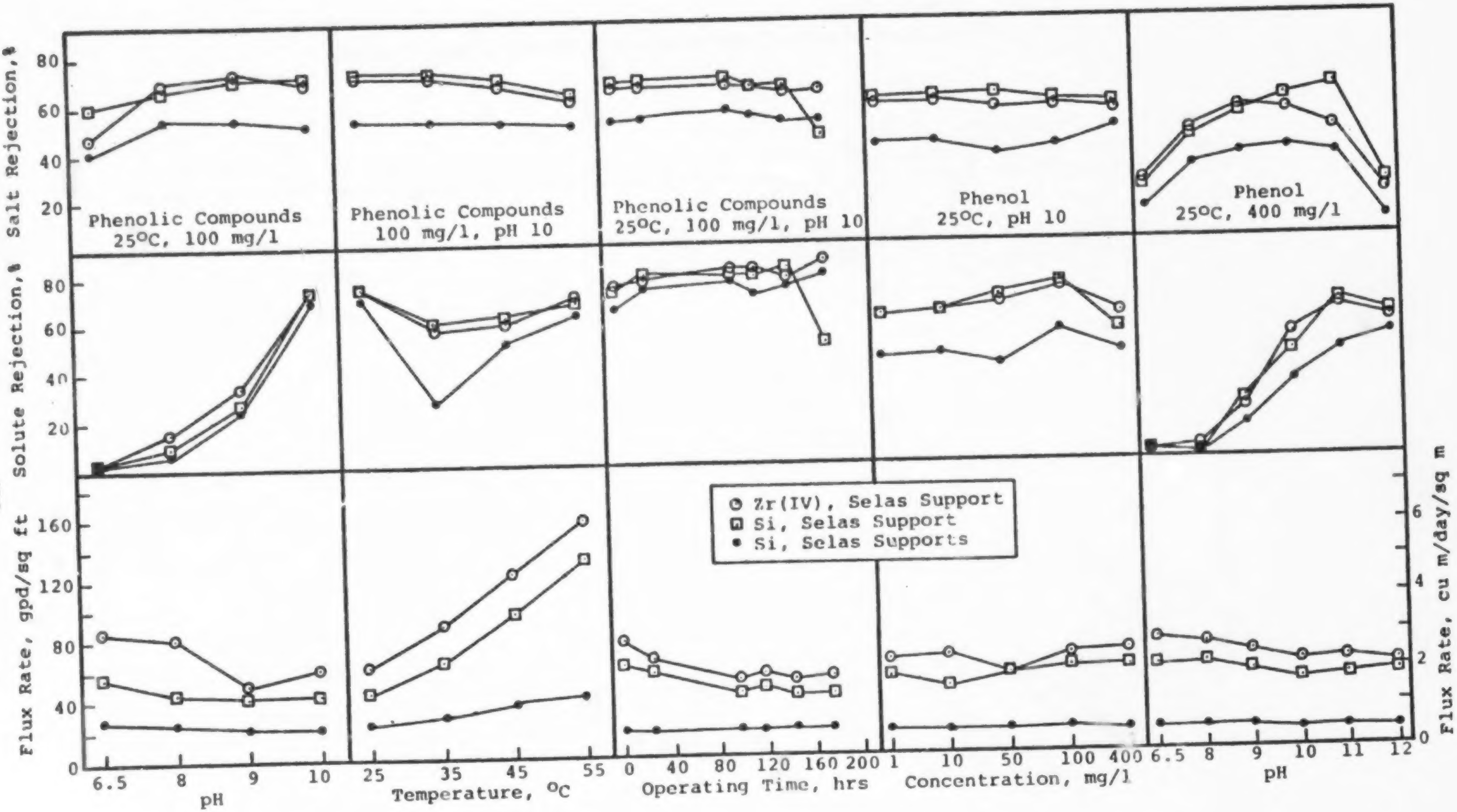

Figure 6. Ultrafiltration of phenolic compounds and phenol (200 psig, 1.38 MPa).

3. Increasing the pressure of the feed significantly increased the flux rate but had little effect on the solute and salt rejection rates.
4. Variations in concentration produced little change in rejection rates but did cause a slight decrease in flux rates as concentration increased.
5. Long-time operation of the processes indicated that the rejection rates and flux rates stabilize after a short period of time.
6. Increasing the temperature of the feed resulted in an increase in the flux rate but very little change in the rejection rates.
7. The best rejection of the phenolic compounds was obtained with a pH of 10, pressure of 950 psig (6.5 MPa), and zirconium oxide-polyacrylic acid on carbon supports.

ACKNOWLEDGMENTS

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COMPOSITION AND BIODEGRADABILITY OF ORGANICS IN COAL CONVERSION WASTEWATERS

Philip C. Singer, Frederic K. Pfaender,
Jolene Chinchilli, and James C. Lamb, III

Department of Environmental Sciences
and Engineering
School of Public Health
University of North Carolina
Chapel Hill, North Carolina 27514

INTRODUCTION

Several technologies for producing synthetic fuels from coal are under development. While most of the emphasis has centered upon development of efficient process technology to produce high energy, clean, synthetic fuels, little information is available with respect to the nature of the waste materials produced and the environmental impact of byproduct waste streams from the various gasification and liquefaction processes.

Wastewaters from coal conversion processes can originate from a variety of sources depending upon the specific processes employed. The composition of the wastewater depends upon the process technology, operating conditions, and nature of the feed coal. Some characteristics of these wastewaters are shown in Table 1. Many coal conversion technologies employ byproduct recovery systems for phenol and ammonia, two of the major constituents of the wastewater as shown in the table. Phenol concentrations in the solvent-extracted liquor, however, are still appreciable and further treatment of the waste streams is still required.

Most coal conversion technologies incorporate or project aerobic biological waste treatment processes (e.g., activated sludge, aerated lagoons, etc.) as the principal means of treating the residual phenol and other organic impurities in the wastewater. However, the nature and biodegradability of these other organic materials, which are included in Table 1 as part of the COD (chemical oxygen demand) are not known. Hence, the extent to which these COD components can be removed by biological treatment cannot be predicted.

Since even well-operated biological treatment processes typically remove only 85-95 percent of the influent BOD (biochemical oxygen demand) and a significant portion of the wastewater organics may not even be biodegradable, it is doubtful that biological treatment alone can provide an environmentally acceptable discharge.

In view of these considerations, a need exists:

a. to identify the nature and characteristics of aqueous discharges from coal conversion processes and to assess their environmental impact, and
b. to develop satisfactory means for the treatment of these wastewaters in order that they may be disposed of in an environmentally acceptable fashion.

Accordingly, this paper presents the results of a survey aimed at determining the chemical characteristics of coal conversion wastewaters and at identifying specific organic contaminants which might be found in such wastewaters. The constituents have been identified by reviewing the published literature, visiting coal gasification and liquefaction research and demonstration installations, and analyzing reports and project documents from a variety of coal conversion operations. A preliminary assessment of the aquatic impact of these wastewaters and of their biological treatability is also presented.

CHARACTERISTICS OF COAL CONVERSION WASTEWATERS

Table 1, presented earlier, shows the results of an analysis conducted by Forney, et al., (1974)[1] of the condensate wastewater generated from the Synthane gasification of six different types of coal. The wastewater characteristics of the weak ammonia liquor from a coke plant are also presented for purposes of comparison. The waste condensate streams appear to be somewhat alkaline and contain rather substantial amounts of ammonia. The concentration of organic material, represented by the chemical oxygen demand (COD), appears to consist, for the most part, of phenol.

TABLE 1

BYPRODUCT WATER ANALYSIS FROM SYNTHANE GASIFICATION OF VARIOUS COALS. (AFTER FORNEY ET AL. (1974).[1])

(ALL VALUES IN mg/l EXCEPT pH.)

	Coke Plant	Illinois No. 6 Coal	Wyoming Subbituminous Coal	Illinois Char	North Dakota Lignite	Western Kentucky Coal	Pittsburgh Seam Coal
pH	9	8.6	8.7	7.9	9.2	8.9	9.3
Suspended Solids	50	600	140	24	64	55	23
Phenol	2,000	2,600	6,000	200	6,600	3,700	1,700
COD	7,000	15,000	43,000	1,700	38,000	19,000	19,000
Thiocyanate	1,000	152	23	21	22	200	188
Cyanide	100	0.6	0.23	0.1	0.1	0.5	0.6
NH_3	5,000	8,100	9,520	2,500	7,200	10,000	11,000
Chloride	-	500	-	31	-	-	-
Carbonate	-	6,000	-	-	-	-	-
Bicarbonate	-	11,000	-	-	-	-	-
Total Sulfur	-	1,400	-	-	-	-	-

TABLE 2

PERCENTAGE OF COD ATTRIBUTABLE TO PHENOL IN SYNTHANE GASIFICATION BYPRODUCT WATER. (RAW DATA FROM FORNEY ET AL. (1974).[1]

Component	Sample*						
	1	2	3	4	5	6	7
Chemical Oxygen Demand, mg/1	7,000	15,000	43,000	1,700	38,000	19,000	19,000
Phenol, mg/1	2,000	2,600	6,000	200	6,600	3,700	1,700
Phenol, mg/1 equiv. of COD	4,760	6,188	14,280	476	15,708	8,806	4,046
Phenol, % of COD	68.0	41.2	33.2	28.0	41.3	46.3	21.3

*Column 1 contains wastewater data from a coke plant; Columns 2-7 contain wastewater data from the gasification of several different types of coals (see Table 1).

Table 2 indicates, however, that phenol accounts for only 21 to 46 percent of the COD in the condensate samples; the remaining 54 to 79 percent of the COD is apparently due to the presence of other organic components of the waste streams. Table 2 was developed by calculating the COD-equivalent of the phenol concentrations given in Table 1, using a stoichiometric factor of 2.38 g of COD per g of phenol from the equation

$$\underset{\text{phenol}}{C_6H_5OH} + 7\,O_2 \rightarrow 6CO_2 + 3H_2O \quad (1)$$

Bromel and Fleeker (1976)[2] examined some general properties of raw and processed wastewater from the Lurgi process plant at Sasolburg, South Africa. Table 3 shows that the raw Lurgi wastewater is similar to that from Synthane in terms of its alkaline pH and high ammonia and COD concentrations. The raw wastewater consists of the condensate from the gasifier (gas liquor) after tar and oil separation. The processed wastewater refers to the gas liquor following phenol and ammonia extraction.

In order to determine the nature of the organic species comprising the COD and total organic carbon (TOC), Bromel and Fleeker conducted a series of chromatographic separations and identified and quantified the components reported in Table 4. It is apparent that, of the specific organic compounds identified, phenol and its methyl substituents, the cresols (methylphenols) and xylenols (dimethylphenols), are the major organic components of the condensate. Polyhydric phenols were not analyzed for. The other major classes identified are the fatty acids (aliphatic acids) and the aromatic amines consisting of pyridine and its methyl derivatives, and aniline. Quinoline and alkyl amines were found in lesser amounts. It is apparent from the table that the phenol extraction step is relatively efficient in separating the monohydric phenols and even the aromatic amines from the gas liquor.

In order to determine what fraction of the COD and TOC reported in Table 3 could be accounted for by the specific organics identified in Table 4, a series of calculations was performed to determine the COD and TOC-equivalents of the compounds listed in Table 4. The basis for these calculations is shown in Table 5, and the TOC and COD-equivalents of the organic constituents are listed in Table 6. In the raw wastewater, the total COD of the constituents listed is 6738 mg/l of which the monohydric phenols comprise 5915 mg/l. The

TABLE 3

SOME GENERAL PROPERTIES OF RAW AND PROCESSED WASTEWATER FROM THE LURGI-PROCESS PLANT AT SASOLBURG, SOUTH AFRICA. (AFTER BROMEL AND FLEEKER (1976).[2])

	Values	
Parameter	Raw Waste Water	Processed Waste Water
Chemical Oxygen Demand (mg/l)	12,500	1,330
Organic Carbon (mg/l)	4,190	ND[A]
Total Dissolved Solids (mg/l)	2,460	596
pH	8.9	8.2
Ammonia (mg/l)	11,200	150

[A] ND, not determined.

TABLE 4

CONCENTRATION OF ORGANIC COMPOUNDS FOUND IN RAW AND PROCESSED WASTEWATER FROM THE LURGI-PROCESS PLANT AT SASOLBURG, SOUTH AFRICA. (AFTER BROMEL AND FLEEKER (1976)[2].)

Compound	Concentration (mg/l) Raw Waste Water	Concentration (mg/l) Processed Waste Water
Fatty Acids		
Acetic Acid	171	123
Propanoic Acid	26	30
Butanoic Acid	13	16
2-Methylpropanoic Acid	2	5
Pentanoic Acid	12	7
3-Methylbutanoic Acid	1	5
Hexanoic Acid	1	8
Monohydric Phenols		
Phenol	1,250	3.2
2-Methylphenol	340	<0.2
3-Methylphenol	360	<0.2
4-Methylphenol	290	<0.2
2, 4-Dimethylphenol	120	NF[A]
3, 5-Dimethylphenol	<50	NF
Aromatic Amines		
Pyridine	117	0.45
2-Methylpyridine	70	<0.05
3-Methylpyridine	26	<0.05
4-Methylpyridine	6	<0.05
2, 4-Dimethylpyridine	<1	NF
2, 5-Dimethylpyridine	<1	NF
2, 6-Dimethylpyridine	<1	NF
Aniline	12	NF

[A] NF, not found.

TABLE 5

COD AND TOC-EQUIVALENTS OF ORGANIC CONSTITUENTS OF SASOL WASTEWATER

Reaction	Chemical Oxygen Demand, gm O_2/gm org.	Total Organic Carbon, gm C/gm org.
Phenol $C_6H_5OH + 7\ O_2 \rightarrow 6CO_2 + 3H_2O$	2.35	0.77
Methylphenol (cresol) $C_7H_8O + 8.5\ O_2 \rightarrow 7CO_2 + 4H_2O$	2.52	0.78
Dimethylphenol (xylenol) $C_8H_{10}O + 10\ O_2 \rightarrow 8CO_2 + 5H_2O$	2.62	0.79
Pyridine $C_5H_5N + 5.5\ O_2 \rightarrow 5CO_2 + H_2O + NH_3$	2.23	0.76
Methylpyridine $C_6H_7N + 7\ O_2 \rightarrow 6CO_2 + 2H_2O + NH_3$	2.41	0.77
Dimethylpyridine $C_7H_9N + 8.5\ O_2 \rightarrow 7CO_2 + 3H_2O + NH_3$	2.54	0.79
Aniline $C_6H_7N + 7\ O_2 \rightarrow 6CO_2 + 2H_2O + NH_3$	2.41	0.77
Acetic Acid $CH_3COOH + 2\ O_2 \rightarrow 2CO_2 + 2H_2O$	1.07	0.40
Propanoic Acid $CH_3CH_2COOH + 3.5\ O_2 \rightarrow 3CO_2 + 3H_2O$	1.51	0.49
Butanoic Acid $CH_3(CH_2)_2COOH + 5\ O_2 \rightarrow 4CO_2 + 4H_2O$	1.82	0.60
Methylpropanoic Acid $C_4H_9O_2 + 21/4\ O_2 \rightarrow 4CO_2 + 9/2\ H_2O$	1.89	0.54
Pentanoic Acid $C_5H_{10}O_2 + 6.5\ O_2 \rightarrow 5CO_2 + 5H_2O$	2.04	0.59
Methylbutanoic Acid $C_5H_{11}O_2 + 27/4\ O_2 = 5CO_2 + 11/2\ H_2O$	2.10	0.58
Hexanoic Acid $C_6H_{12}O_2 + 8\ O_2 = 6CO_2 + 6H_2O$	2.21	0.62

monohydric phenols contribute 1866 mg/l of TOC out of the total TOC of 2143 mg/l accounted for by the indicated constituents. However, if the COD and TOC of the identified organic components of the Sasol wastewater from Table 6 are compared to the total concentrations reported for the same sample in Table 3, Table 7 shows that 46.1 percent of the COD and 48.9 percent of the TOC of the raw wastewater is not accounted for. Similarly, a very small percentage of the COD (and, also probably of the TOC) of the processed wastewater is attributable to the residual aliphatic acids following phenol extraction.

It should be noted that the data presented in Tables 3 and 4 were derived from single samples of the aqueous gas liquor and the phenol-extracted gas liquor. The age of the

TABLE 6

CONCENTRATION OF ORGANIC COMPOUNDS, AS COD AND TOC, FOUND IN THE RAW AND PROCESSED WASTEWATER FROM THE LURGI-PROCESS PLANT AT SASOLBURG, SOUTH AFRICA. RAW DATA FROM BROMEL AND FLEEKER (1976)[2].)

	Concentration, mg/l			
	Raw Wastewater		Processed Wastewater	
Compound	COD	TOC	COD	TOC
Fatty Acids				
acetic acid	183	68.4	131.6	49.2
propanoic acid	39.3	12.7	45.3	14.7
butanoic acid	23.7	7.8	29.1	9.6
2-methylpropanoic acid	3.8	1.1	9.5	2.7
pentanoic acid	24.5	7.1	14.3	4.1
3-methylbutanoic acid	2.1	0.6	10.5	2.9
hexanoic acid	2.2	0.6	17.7	5.0
	278.6	98.3	258	88.2
Monohydric Phenols				
phenol	2975	963	7.6	2.5
2-methylphenol	857	265	<0.5	<0.2
3-methylphenol	907	277	<0.5	<0.2
4-methylphenol	731	226	<0.5	<0.2
2, 4-dimethylphenol	314	95	-	-
3, 5-dimethylphenol	<131	<39.5	-	-
	5915	1866	9.1	3.1
Aromatic Amines				
pyridine	261	88.9	1.0	0.34
2-methylpyridine	169	53.9	<0.12	<0.04
3-methylpyridine	62.7	20.0	<0.12	<0.04
4-methylpyridine	14.5	4.6	<0.12	<0.04
2, 4-dimethylpyridine	<2.5	<0.8	-	-
2, 5-dimethylpyridine	<2.5	<0.8	-	-
2, 6-dimethylpyridine	<2.5	<0.8	-	-
aniline	28.9	9.2	-	-
	544	179	1.4	0.5
TOTAL	6738	2143	269	92

TABLE 7

PERCENTAGES OF UNIDENTIFIED COD AND TOC IN SASOL WASTEWATER (RAW DATA FROM BROMEL AND FLEEKER (1976)[2].)

Parameter	Raw Wastewater	Processed Wastewater
Total COD, mg/l	12,500	1,330
COD of Identified Constituents, mg/l	6,738	269
% of COD Unidentified	46.1	79.8
Total TOC, mg/l	4,190	-
TOC of Identified Constituents, mg/l	2,143	92
% of TOC Unidentified	48.9	-

samples was not accurately known, but is believed to have been less than 6 months for the raw wastewater and less than 1 month for the processed wastewater. The analyses were completed within 4 months following receipt of the samples (Bromel and Fleeker, 1976)[2].

It is apparent from Tables 2 and 7 that many other organic species are present in coal conversion wastewaters, and that a need exists for further identification and quantification of these constituents.

Along these lines, Schmidt, Sharkey, and Friedel (1974)[3] employed mass spectrometric methods to determine the nature of the organic contaminants in condensate waters from the Synthane gasification of coal. (The Synthane process produces about 0.4 - 0.6 tons of condensate water per ton of coal gasified (Forney et al., 1974.[1]) The condensate waters from the gasification of six different coals were extracted with methylene chloride and were identified using high resolution mass spectrometry, combined gas chromatography-mass spectrometry, and low-voltage mass spectrometry. Table 8 summarizes the results of these spectrometric analyses for the six different coals gasified. Again, phenol appears to be the major organic component of the condensate waters and, along with the other monohydric, dihydric,and polyphenols, constitutes approximately 60 to 80 percent of the methylene chloride extract. Several other classes of organics appear to be represented, including heterocyclic compounds such as the pyridines and furans, and polycyclic components such as indenols, indanols, naphthols, quinolines, and indoles. It is interesting to note that, regardless of the type of coal gasified, the composition of the condensate water, in terms of the component organics and their concentrations, is relatively uniform. It should also be noted that the constituents reported by Bromel and Fleeker (1976)[2] in Table 4 are consistent with the listing by Schmidt, Sharkey, and Friedel (1974)[4] in Table 8.

Expanding on this effort to identify organic constituents in wastewaters from coal gasification and coal liquefaction operations from various sources, Table 9 is a summary of information gathered from the eight different references cited. The organics have been grouped into various classes and include monohydric and dihydric phenols, polycyclic hydroxy compounds (polyphenols), monocyclic and polycyclic nitrogen-containing aromatics (including heterocyclic compounds such as the pyridines, quinolines, indoles, acridines and carbazoles, and the aminobenzenes), aliphatic acids, and a group of miscellaneous other compounds. The check (✓) marks indicate that the compound in question has been identified but not quantified. The range notation (↕) indicates that the concentrations given are for a group of compounds, but that the individual components within the group have not been quantified, e.g., 140-1170 mg/l for column 1

TABLE 8

CONTAMINANTS IN PRODUCT WATER FROM SYNTHANE GASIFICATION OF VARIOUS COALS. (AFTER SCHMIDT ET AL. (1974).[3])
(ALL CONCENTRATIONS IN mg/l.)

	Illinois No. 6 (hvBb)		Montana (Sub)	N. Dak. (Lig)	Wyo. (Sub)	W. Ky. (hvBb)	Pgh. (hvAb)
Phenol	3,400	2,660	3,160	2,790	4,050	2,040	1,880
Cresols	2,840	2,610	870	1,730	2,090	1,910	2,000
C_2-Phenols	1,090	780	240	450	440	620	760
C_3-Phenols	110	100	30	60	50	60	130
Dihydrics	250	540	130	70	530	280	130
Benzofuranols	70	100	80	60	100	50	70
Indanols							
Acetophenones	150	100	140	110	110	90	120
Hydroxy-benzaldehyde	60	110	-	-	60	50	80
Benzoic Acids							
Naphthols	160	110	160	140	80	160	170
Indenols	90	90	70	50	60	80	20
Benzofurans	-	-	10	10	-	-	110
Dibenzofurans	-	-	-	-	-	-	-
Biphenols	40	20	-	-	40	20	60
Benzothio-phenols	110	60	-	10	20	70	20
Pyridines	-	60	270	220	120	30	540
Quinolines	-	-	20	10	-	-	10
Indoles	-	20	70	30	20	40	40

TABLE 9

SUMMARY: ORGANIC CONSTITUENTS IN COAL CONVERSION WASTEWATERS (ALL CONCENTRATIONS IN mg/l).

	SYNTHANE TPR-86 (1)	OIL SHALE (2)	SYN-THANE (3)	COED (4)	SRC (5)	LURGI-WESTFIELD (6)	SYN-THANE (7)	LURGI-SASOL (8)	HYDRO-CARBONIZ. (9)	COED (10)
MONOHYDRIC PHENOLS										
PHENOL	1000-4480	10	2100	2100	✓	1250-3100		1250		
o-CRESOL		30	670	650	✓	153-343	2209	340		
m-CRESOL	530-3580				✓	170-422		360		
p-CRESOL		20	1800	1800	✓	160-302		290		
2, 6-XYLENOL			40	30	✓					
3, 5-XYLENOL			230	240	✓			50		
2, 3-XYLENOL			30	40						
2, 5-XYLENOL	140-1170		250	220	✓	100-393				
3, 4-XYLENOL			100	900			2185			
2, 4-XYLENOL			-	-	✓			120		
o-ETHYLPHENOL			30	30	✓					
m-ETHYLPHENOL					✓					
p-ETHYLPHENOL					✓					
3-METHYL, 6-ETHYLPHENOL					✓					
2-METHYL, 4-ETHYLPHENOL					✓					
4-METHYL, 2-ETHYLPHENOL	20-150				✓					
5-METHYL, 3-ETHYLPHENOL					✓		66			
2, 3, 5-TRIMETHYLPHENOL					✓					
c-ISOPROPYLPHENOL	✓						40			
DIHYDRIC PHENOLS										
CATECHOL	✓				✓	190-555			1700	✓
3-METHYLCATECHOL					✓	30-394				✓
4-METHYLCATECHOL						110-385				✓
3, 5-DIMETHYLCATECHOL						✓				
3, 6-DIMETHYLCATECHOL						0-45				
METHYLPYROCATECHOL	✓									
RESORCINOL	✓				✓	176-272			2000	✓
5-METHYLRESORCINOL					✓	40-64			2000	✓
4-METHYLRESORCINOL						0-36			2000	
2-METHYLRESORCINOL					✓					✓
2, 4-DIMETHYLRESORCINOL						✓				
HYDROQUINONE	✓								4-7	
POLYCYCLIC HYDROXY COMPOUNDS										
α -NAPHTHOL			10							
β -NAPHTHOL	30-290		30							
METHYLNAPHTHOL										
INDENOL	20-110									
C_1-INDENOL										
4-INDANOL	40-150						66			
C_1-INDANOL										
BIPHENOL	0-110									

TABLE 9 (Continued)

	SYNTHANE TPR-86 (1)	OIL SHALE (2)	SYN-THANE (3)	COED (4)	SRC (5)	LURGI-WESTFIELD (6)	SYN-THANE (7)	LURGI-SASOL (8)	HYDRO-CARBONIZ. (9)	COED (10)
MONOCYCLIC N-AROMATICS										
PYRIDINE	30-580							117		
HYDROXYPYRIDINE									10	
METHYLHYDROXYPYRIDINE									10	
METHYLPYRIDINE							✓	104		
DIMETHYLPYRIDINE							5	<1	20	
ETHYLPYRIDINE										
C_3-PYRIDINE										
C_4-PYRIDINE										
ANALINE							21	12		
METHYLANILINE							9			
DIMETHYLANILINE							11			
POLYCYCLIC N-AROMATICS										
QUINOLINE	0-100				✓		7			
METHYLQUINOLINE					✓		27			
DIMETHYLQUINOLINE					✓					
ETHYLQUINOLINE					✓					
BENZOQUINOLINE					✓					
METHYLBENZOQUINOLINE					✓					
TETRAHYDROQUINOLINE					✓					
METHYLTETRAHYDROQUINOLINE					✓					
ISOQUINOLINE					✓					
INDOLE	0-110				✓		63			
METHYLINDOLE					✓					
DIMETHYLINDOLE					✓					
BENZOINDOLE					✓					
METHYLBENZOINDOLE					✓					
CARBAZOLE					✓					
METHYLCARBAZOLE					✓				4	
ACRIDINE					✓					
METHYLACRIDINE					✓					

TABLE 9 (Continued)

	Synthane TPR-86 (1)	Oil Shale (2)	Syn-thane (3)	COED (4)	SRC (5)	Lurgi-Westfield (6)	Syn-thane (7)	Lurgi-Sasol (8)	Hydro-carboniz. (9)	COED (10)
Aliphatic Acids										
Acetic Acid		600	620	600				171		
Propanoic Acid		210	60	90				26		
n-Butanoic Acid		130	20	40				13		
2-Methylpropanoic Acid		-	-	-				2		
n-Pentanoic Acid		200	10	30				12		
3-Methylbutanoic Acid		-	-	-				1		
n-Hexanoic Acid		250	20	30				1		
n-Heptanoic Acid		260	-	-						
n-Octanoic Acid		250	-	-						
n-Nonanoic Acid		100	-	-						
n-Decanoic Acid		50	-	-						
Others										
Benzofurans	10-110									
Benzofuranols	50-100									
Benzothiophenols	10-110									
Acetophenones	90-150									
Hydroxybenzaldehyde or Benzoic Acid	50-110									

for the C_2-phenols which include the isomers of xylenol (dimethylphenol) and ethylphenol. Where a range of values is given, e.g., 1000-4480 mg/l for phenol in column 1, this indicates that several samples have been analyzed and the concentrations measured are within the given range.

Column 1 is derived from the previously discussed methylene-chloride, mass spectrometric analysis by Schmidt, Sharkey, and Friedel (1974)[3] for the condensate waters from the Synthane gasification of six different types of coal under different process conditions. Columns 2, 3, and 4 include date from Ho, Clark, and Guerin (1976)[4] and were obtained by gas chromatography using Tenax columns and flame ionization detection. Identifications were made from comparisons of the chromatograms with retention time data for reagent grade compounds. Some identifications were confirmed by gas chromatography-mass spectrometry. Quantitation was made by integrating peak areas from the chromatogram and comparing with standards of known concentration. The oil shale byproduct water (column 2) was obtained by centrifugation of an oil/water emulsion product from a simulated in-situ retort run made by the Laramie (Wyoming) Energy Research Center. The gasification byproduct water (column 3) was a sample of filtered condensate water from the Synthane process, provided by the Pittsburgh (Pennsylvania) Energy Research Center. The coal liquefaction byproduct sample (column 4) was filtered water from the first-stage gas scrubber of the COED (Char Oil Energy Development) liquefaction process, provided by FMC Corporation, of Princeton, New Jersey.

The information in column 5 was obtained from a characterization of organics in coal-derived liquids from the Ft. Lewis, Washington Solvent Refined Coal Plant by Fruchter et al., (1977).[5] The constituents of the raw process water were separated into acidic, basic, neutral, and polyaromatic fractions and each fraction was separated further by gas chromatography. Gas chromatography/mass spectrometry was then employed to identify the components. The constituents indicated in column 5 have been positively identified, but not yet quantified.

Column 6 contains data collected by Janes and Rhodes (1977)[6] from the Lurgi gasification facility in Westfield, Scotland. The data were obtained for tar water and oil water samples from old plant records, and the analytical and sample-handling procedures were not reported. Nevertheless, the constituents and the concentrations appear to be consistent with the other reports.

Column 7 is derived from an M.S. thesis by Spinola (1976)[7] and contains data for a condensate sample from the Synthane gasification of an Illinois No. 6 coal. The organic content was analyzed by direct gas chromatography of acidic and basic fractions and identification was based on relative retention time data.

The data in column 8 for the Lurgi facility in Sasolburg, South Africa is from the report by Bromel and Fleeker (1976)[2] discussed above in connection with Tables 3-7.

The information in column 9 is from an analysis by Jolley, Pitt, and Thompson (1977)[8] of an aqueous stream from the product scrubber of a bench-scale hydrocarbonization coal liquefaction operation. The samples were analyzed by high pressure liquid chromatography, and the separated constituents were identified by a multiple analytical procedure involving gas chromatography and mass spectrometry.

Column 10 cites specific organics identified in an aqueous sample from the product separator (2nd stage liquor) of the COED coal liquefaction pilot plant (Shults, 1976).[9] The constituents were separated by high resolution anion exchange chromatography, and a variety of different analytical techniques were employed for identification and quantification.

With reference to the material contained in Table 9, it is important to note that the components identified and the concentrations reported are from grab samples of process streams collected from the various facilities and locations cited. The analyses are not complete, and the fact that they are analyses of grab samples from processes still under development means that the concentrations may not be truly representative of on-line, commercial, steady-state gasification and liquefaction operations. Additionally, the number and type of organic compounds listed are limited, in part, by the analytical methodologies employed for extracting, separating, and identifying the constituents of the waste streams.

While it might have been predicted, a priori, that the composition of wastewaters from coal conversion facilities would vary depending upon the specific process technology (operating temperature and pressure, mode of contact between coal and steam, process sequence, gas cleanup and separation technology, etc.) and type of feed coal employed, Table 9 suggests that the composition of coal gasification and liquefaction wastewaters is relatively uniform, especially with respect to the phenolic constituents. Less information is available regarding the presence of specific N-containing aromatics, other polycyclic and heterocyclic compounds, and polynuclear aromatic hydrocarbons. Table 10 lists some of the PAH's identified by Fruchter et al., (1977)[5] in the raw process wastewater from the Solvent-Refined Coal facility in Ft. Lewis, Washington, but the quantification and widespread occurrence of these PAH's in coal conversion wastewaters have not been established.

In any case, the similarity in composition of coal conversion wastewaters from different developing technologies suggests that the environmental impact of such wastewaters from

TABLE 10

POLYNUCLEAR AROMATIC HYDROCARBONS IN SRC RAW PROCESS WATER. (AFTER FRUCHTER ET AL. (1977).[5])

PNA	CONCENTRATION (mg/l)	IDENTIFIED BUT NOT YET QUANTITATED
METHYLINDANE	15	METHYLPYRENE
TETRALIN	<0.1	BENZOFLUORENE
DIMETHYLTETRALIN	0.5	C_2-PYRENE
NAPHTHALENE	5	C_2-FLUORANTHENE
2-NAPHTHALENE	2	TETRAHYDROCHRYSENE
DIMETHYLNAPHTHALENE	0.3-2	CHRYSENE
2-ISOPROPYLNAPHTHALENE	0.7	METHYLBENZOFLUORENE
1-ISOPROPYLNAPHTHALENE	2	C_3-PYRENE
BIPHENYL	0.2	C_3-FLUORANTHENE
ACENAPHTHALENE	<0.1	METHYLCHRYSENE
DIMETHYLBIPHENYL	0.2-0.5	METHYLBENZANTHRACENE
DIBENZOFURAN	0.6	CHOLANTHRENE
XANTHENE	0.1	TETRAHYDROBENZOFLUORANTHENE
DIBENZOTHIOPHENE	1.5	TETRAHYDROBENZOPYRENE
METHYLDIBENZOTHIOPHENE	<0.1	BENZOPYRENE
DIMETHYLDIBENZOTHIOPHENE	<0.05	METHYLBENZOPYRENE
THIOXANTHENE	0.1	METHYLBENZOFLUORANTHENE
FLUORENE	0.3	BENZOFLUORANTHENE
9-METHYLFLUORENE	0.3	
1-METHYLFLUORENE	0.2	
ANTHRACENE/PHENANTHRENE	1.1	
METHYLPHENANTHRENE	0.2-0.3	
C_2-ANTHRACENE	<0.05	
FLUORANTHENE	0.4	
DIHYDROPYRENE	<0.05	
PYRENE	0.6	

different sources, and the treatability of these wastewaters will be similar.

AQUATIC IMPACT OF ORGANIC CONSTITUENTS OF COAL CONVERSION WASTEWATERS

Although there is general agreement that most coal conversion processes will produce relatively contaminated wastewaters, little data are available concerning the biological impact such wastes will have upon receiving waters. The lack of information reflects the fact that coal conversion technology has only recently emerged, and no commercial systems have yet been constructed in the United States. As such, efforts to assess the environmental impact of coal conversion wastewaters are in a predictive rather than descriptive stage. While ultimate evaluation of the environmental impact of these streams must await the construction and continuous operation of large scale conversion systems, interim predictive efforts are mandated by the number of highly toxic, carcinogenic, and mutagenic compounds known or anticipated to occur in coal conversion wastes.

Currently, prediction of the impact that coal conversion wastewaters will have on aquatic environments can only be based on a knowledge of the impact of effluents thought to be similar in composition to such wastewaters, or from an analysis of toxicity data on the constituents of the wastes. Towards this latter end, Table 11 shows threshold concentrations of various phenolic constituents of coal conversion wastewaters to selected lower aquatic organisms. If these threshold concentrations are compared to the wastewater concentrations shown in Table 9, it is obvious that a substantial level of wastewater treatment must be accomplished before the discharge can be considered acceptable from an aquatic impact point of view.

Estimated permissible concentrations for a number of hazardous pollutants were recently calculated and compiled by Cleland and Kingsbury (1977).[11] Ambient level goals (see Table 12) were calculated based upon estimated permissible concentrations in order to avoid detrimental health and ecological effects, and emission level goals (see Table 13) were computed based upon treatment technology and the ambient level goals. Several

TABLE 11

THRESHOLD CONCENTRATIONS OF VARIOUS PHENOLICS TO LOWER AQUATIC ORGANISMS (mg/l) (AFTER MCKEE AND WOLF (1963).[10])

COMPOUND	DAPHNIA (MICROCRUSTACEAN)	MICROREGMA (PROTOZOAN)	SCENEDESMUS (ALGA)	E. COLI (BACTERIUM)
PHENOL	16.0	30.0	40.0	>1000
o-CRESOL	16.0	50.0	40.0	600
m-CRESOL	28.0	20.0	40.0	600
p-CRESOL	12.0	10.0	6.0	>1000
3, 4-XYLENOL	16.0	10.0	40.0	500
2, 4-XYLENOL	24.0	70.0	40.0	>100
2, 5-XYLENOL	10.0	50.0	40.0	>100
RESORCINOL	0.8	40.0	60.0	>1000
HYDROQUINONE	0.6	2.0	4.0	50
PYROCATECHOL	4.0	6.0	6.0	90
QUINONE	0.4	2.0	6.0	50

TABLE 12

AMBIENT LEVEL GOALS FOR KNOWN CONSTITUENTS OF COAL CONVERSION WASTEWATERS. CONCENTRATION IN μg/l. (AFTER CLEVELAND AND KINGSBURY, (1977.[11])

COMPOUND	CURRENT OR PROPOSED AMBIENT STANDARDS OR CRITERIA		TOXICITY BASED ESTIMATED PERMISSIBLE CONCENTRATION		ZERO THRESHOLD POLLUTANTS ESTIMATED PERMISSIBLE CONCENTRATION
	BASED ON HEALTH EFFECTS	BASED ON ECOLOGICAL EFFECTS	BASED ON HEALTH EFFECTS	BASED ON ECOLOGICAL EFFECTS	BASED ON HEALTH EFFECTS
PHENOL	1	100			
CRESOLS	1	1-100			
XYLENOLS	1	100			
ALKYL CRESOLS	1	100			
CATECHOL	1	100			
INDANOLS	1	100			
PYRIDINE		<5000	207		
METHYL PYRIDINES			316		
QUINOLINE		<500	14		
METHYL QUINOLINE			492		
ACRIDINE			800		
INDOLE			400		
CARBAZOLE			80		
ANILINE			69		
METHYL ANILINE			303.6		3.9
DIMETHYLANILINE			345		

known constituents of coal conversion wastewaters were included, as shown. The number of categories for which no data exist illustrates the limited amount of information available concerning health and ecological effects of coal conversion wastewater constituents. The few standards based upon ecological effects are limited to the phenolics; in all cases, these standards are derived from concentrations that produce tainting of fish flesh. The lack of information in Table 13 regarding best treatment technology reflects the fact that treatment standards are currently based on gross organic parameters such as BOD, COD, and TOC, and generally not on individual constituents even if these constituents are known or suspected aquatic toxicants or carcinogens. Additionally, the treatment standards have generally been developed for standard industrial categories and, to date, no such category has been established for coal conversion wastewaters.

The report by Cleland and Kingsbury is not complete, and is currently being expanded. Nevertheless, comparisons between the concentrations listed in Tables 12 and 13, and those reported in Table 9 again support the need for a relatively substantial degree of wastewater treatment in order to achieve an environmentally acceptable discharge.

In addition to the specific organic constituents of concern, as discussed above, it is significant to note the high concentrations of oxygen-demanding impurities (as implied by the high COD) associated with these wastewaters (see Tables 1 and 3). These

TABLE 13

EMISSION LEVEL GOALS FOR KNOWN CONSTITUENTS OF COAL CONVERSION WASTEWATERS. CONCENTRATIONS IN μg/l. (AFTER CLELAND AND KINGSBURY, (1977.[11])

COMPOUND	BASED ON BEST TECHNOLOGY		BASED ON AMBIENT FACTORS
	EXISTING TECHNOLOGY BPT	DEVELOPING TECHNOLOGY BAT	AMBIENT LEVEL GOAL
PHENOL			1-100
CRESOLS			1
XYLENOLS			1-100
ALKYL CRESOLS			1-100
CATECHOL			1-100
INDANOLS			1-100
PYRIDINE			207
METHYL PYRIDINES			-
QUINOLINE			14-500
ISOQUINOLINE			
METHYL QUINOLINE			-
ACRIDINE			3
INDOLE			-
CARBAZOLE			-
NAPHTHALENE			690-3800

oxygen-demanding impurities result in the depletion of dissolved oxygen in the receiving water, thereby making the water unsuitable for many types of aquatic organisms, including fish. From this standpoint alone, a significant degree of wastewater treatment is required.

BIODEGRADABILITY OF ORGANIC CONSTITUENTS OF COAL CONVERSION WASTEWATERS

In considering various alternatives for the treatment of coal conversion wastewaters, it is likely that aerobic biological treatment processes, such as activated sludge systems or aerated lagoons, will play a significant role in the overall treatment scheme. In order to assess the feasibility of using such biological processes for treating coal conversion wastewaters, it is first necessary to determine if the constituents of the wastewaters are biologically degradable and, if so, whether or not the wastewater as a whole is biologically treatable, given the actual concentrations of the constituents. In conventional biodegradability studies, very low concentrations (5-10 mg/l) of the test compound are often used in order to avoid the problem of toxicity. While the test compound might prove to be biodegradable under these circumstances, the compound might be toxic to microorganisms at the concentration level at which it is found in the wastewater of interest.

Of the many compounds that are listed in Table 9 as constituents of coal conversion effluents, the microbial degradation of only one class of these compounds, the phenolics, has been extensively investigated. However, review of this work provides information about the microbial degradation of aromatic compounds in general, since phenols are major intermediates in the degradation of aromatics. Therefore, an understanding of the metabolism of phenols is basic to the study of the degradation of other aromatic compounds. Additionally, phenolic compounds comprise the major portion of the total organic carbon content of coal conversion effluents.

It is important to note, however, that the majority of the work on microbial degradation of these organic compounds and the identification of metabolic pathways has been done with pure cultures and single substrates, under highly controlled laboratory conditions. The microbial cultures employed were often maintained and manipulated solely for the purpose of degrading a particular substrate. It is therefore important to recognize that the degradation of a compound under these conditions does not imply that it will be readily biodegradable in a natural or waste treatment situation. Also, lack of degradation or pathway information does not necessarily mean that the compound is not biodegradable, as many compounds identified in coal conversion wastewaters have not been studied.

Many bacteria and fungi can utilize aromatic hydrocarbons as a sole source of carbon and energy. Specialized metabolic pathways convert initial aromatic substrates to aliphatic cellular intermediary metabolites. The initial reaction in the bacterial oxidation of aromatic hydrocarbons is believed to be the formation of *cis*-dihydrodiols (Gibson, 1976).[12] These compounds then undergo further oxidation to yield dihydric phenols which are substrates for ring fission enzymes. This process has been demonstrated for compounds ranging in size from benzene to benzo(a)pyrene.

It is generally recognized that metabolism of benzenoid compounds is dependent on the presence of molecular oxygen. While molecular oxygen acts as a terminal electron acceptor, it is also a specific substrate for those enzymes which catalyze the introduction of hydroxyl groups and the fission of suitably hydroxylated rings. Therefore, such pathways are strictly aerobic.

In order for ring cleavage to occur, the primary substrate must initially be converted to either an *ortho* or *para* dihydric phenol. Two of the most important of these compounds are catechol and protocatechuic acid, both *ortho* dihydric phenols. Figure 1 shows initial sequences for bacterial metabolism of various substrates that converge on catechol, including phenol. The initial metabolism of m- and p-cresols along with other benzenoid compounds may result in the formation of protocatechuic acid. Figure 2 illustrates the convergence of some aromatic hydrocarbons on this ring fission substrate.

The third important ring cleavage substrate is gentisic acid. This is a *para*-dihydric phenol formed from such primary substrates as β-naphthol (see Figure 3).

The importance of the position of the two hydroxyl groups on the ring should not be overlooked. For example, in the metabolism of resorcinol (a *meta*-dihydric phenol), ring fission does not occur until the compound is first hydroxylated to form a 1, 2, 4-trihydric phenol (Ribbons and Chapman, 1968; Chapman and Ribbons, 1976).[13,14]

The modification of a substituent group may or may not occur before ring cleavage depending on bacterial species, nature of the primary substrate and position on the ring relative to other substituents. In the case of the methyl group, some species of bacteria hydroxylate the nucleus of cresols leaving the methyl group intact (Bayly et al., 1966),[15] while others oxidize the methyl group initially to a carboxyl group (Hopper and Chapman, 1971).[16] In the former case the fission substrate is then a methyl-catechol, whereas in the latter case the intermediate formed is either gentisic or protocatechuic acid. The dimethylphenols (xylenols) act similarly. Depending on the position of the methyl groups on the ring, metabolism results in either protocatechuic acid or a methylgentisic acid (Hopper and Chapman, 1971; Chapman and Hopper, 1968).[16,17]

Alkyl side chains possessing two or more carbons may also undergo modification. Carboxylic acids are formed by the oxidation of the terminal methyl group. The larger carboxylic alkyl chains may then undergo β-oxidation, but sometimes may remain intact on the ring cleavage substrates. Generally, carboxyl groups remain intact prior to ring cleavage, but they may be eliminated as in the metabolism of benzoic acid to catechol (Reiner and Hegeman, 1971).[18]

Once the primary substrate has been converted to one of the ring fission substrates,

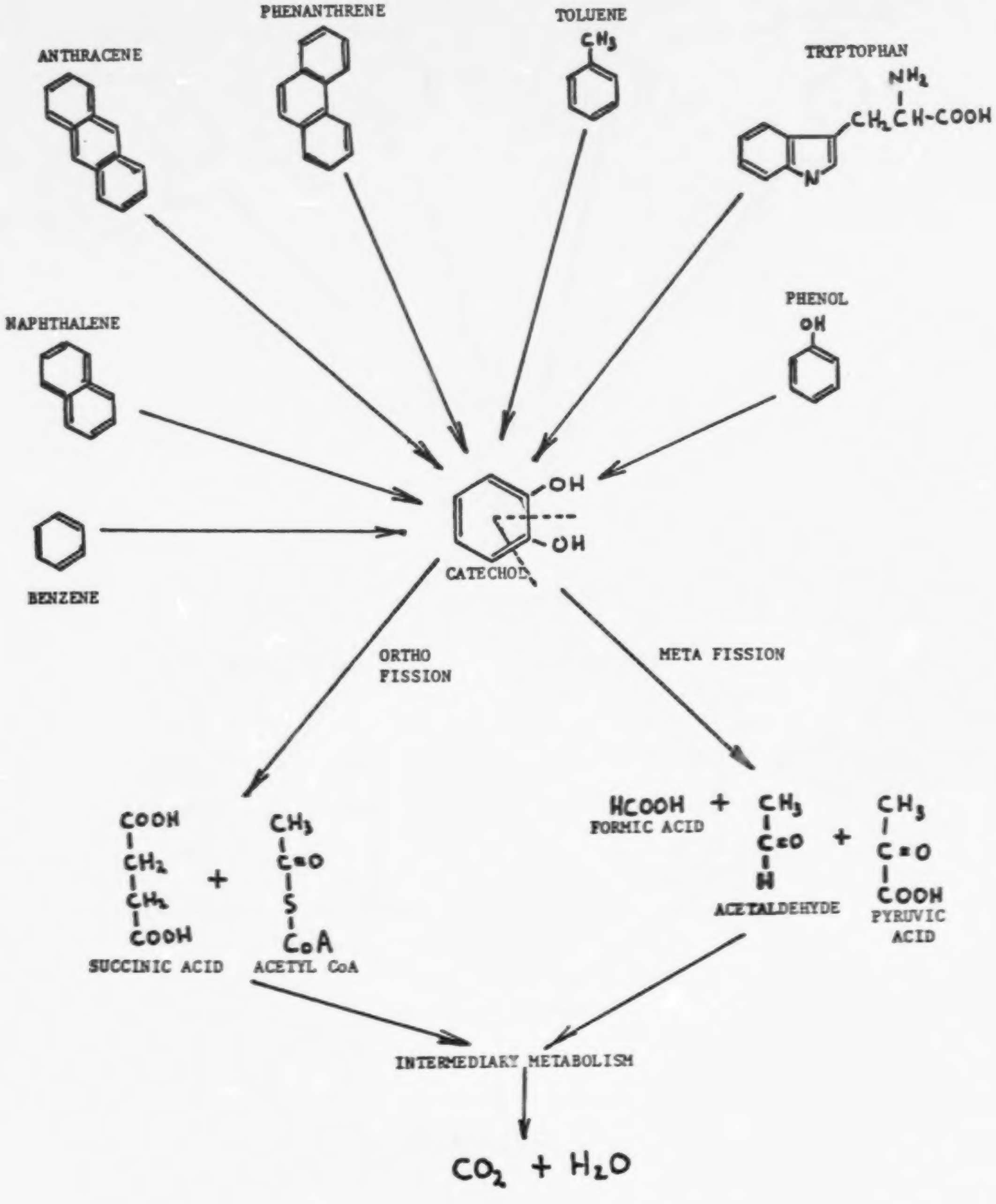
ANTHRACENE
PHENANTHRENE
TOLUENE
CH3
TRYPTOPHAN
NH2
CH2CH-COOH
N
NAPHTHALENE
PHENOL
OH
OH
OH
CATECHOL
BENZENE
ORTHO FISSION
META FISSION
COOH
CH2
CH2
COOH
SUCCINIC ACID
CH3
C=O
S
CoA
ACETYL CoA
HCOOH
FORMIC ACID
CH3
C=O
H
ACETALDEHYDE
CH3
C=O
COOH
PYRUVIC ACID
INTERMEDIARY METABOLISM
CO2 + H2O

Figure 1. Schematic diagram illustrating catechol as a primary ring fission substrate in the microbial metabolism of various aromatic compounds.

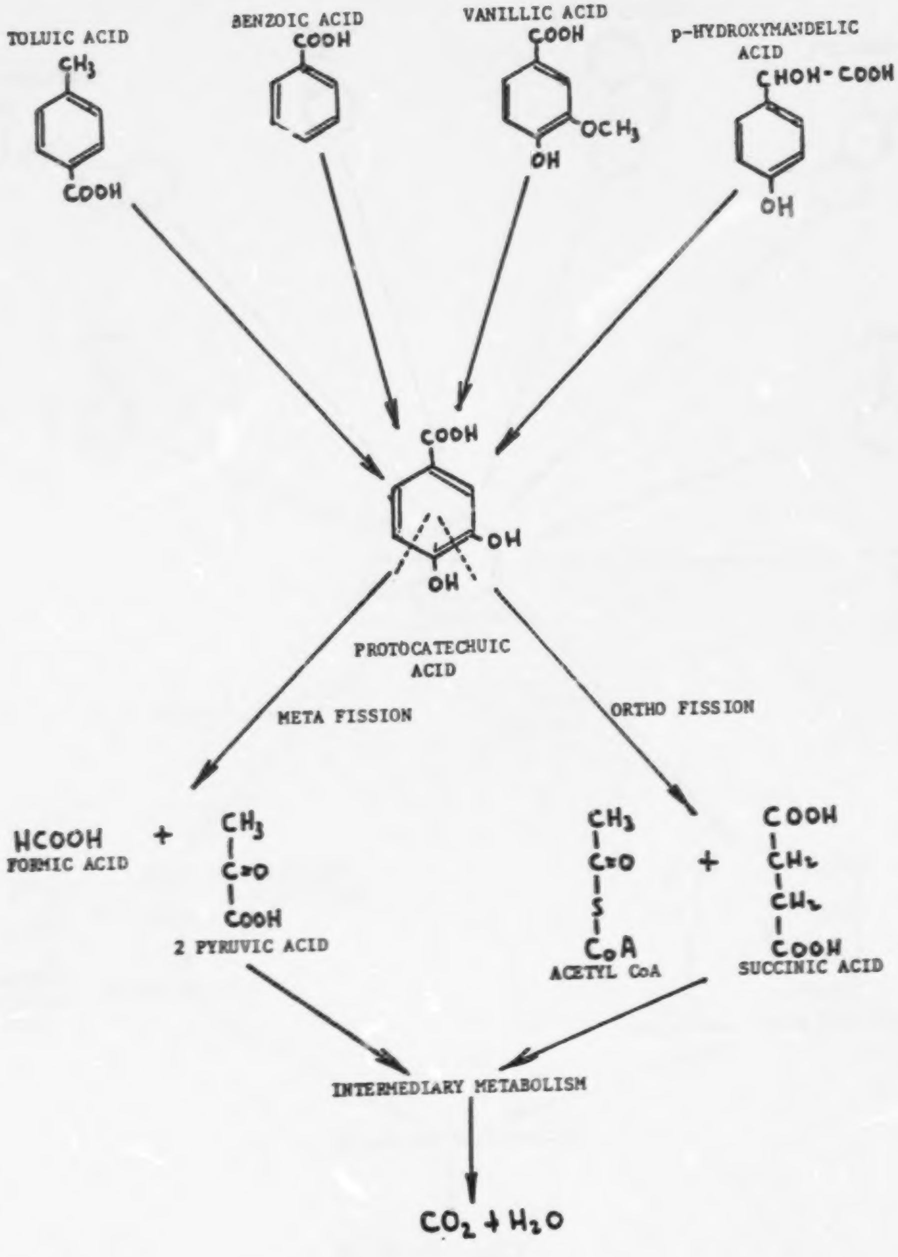
TOLUIC ACID
BENZOIC ACID
VANILLIC ACID
p-HYDROXYMANDELIC ACID
CH_3
COOH
OCH_3
OH
CHOH-COOH
PROTOCATECHUIC ACID
META FISSION
ORTHO FISSION
HCOOH
FORMIC ACID
2 PYRUVIC ACID
ACETYL CoA
SUCCINIC ACID
INTERMEDIARY METABOLISM
$CO_2 + H_2O$

Figure 2. Schematic diagram illustrating protocatechuric acid as a primary ring fission substrate in the microbial metabolism of various aromatic compounds.

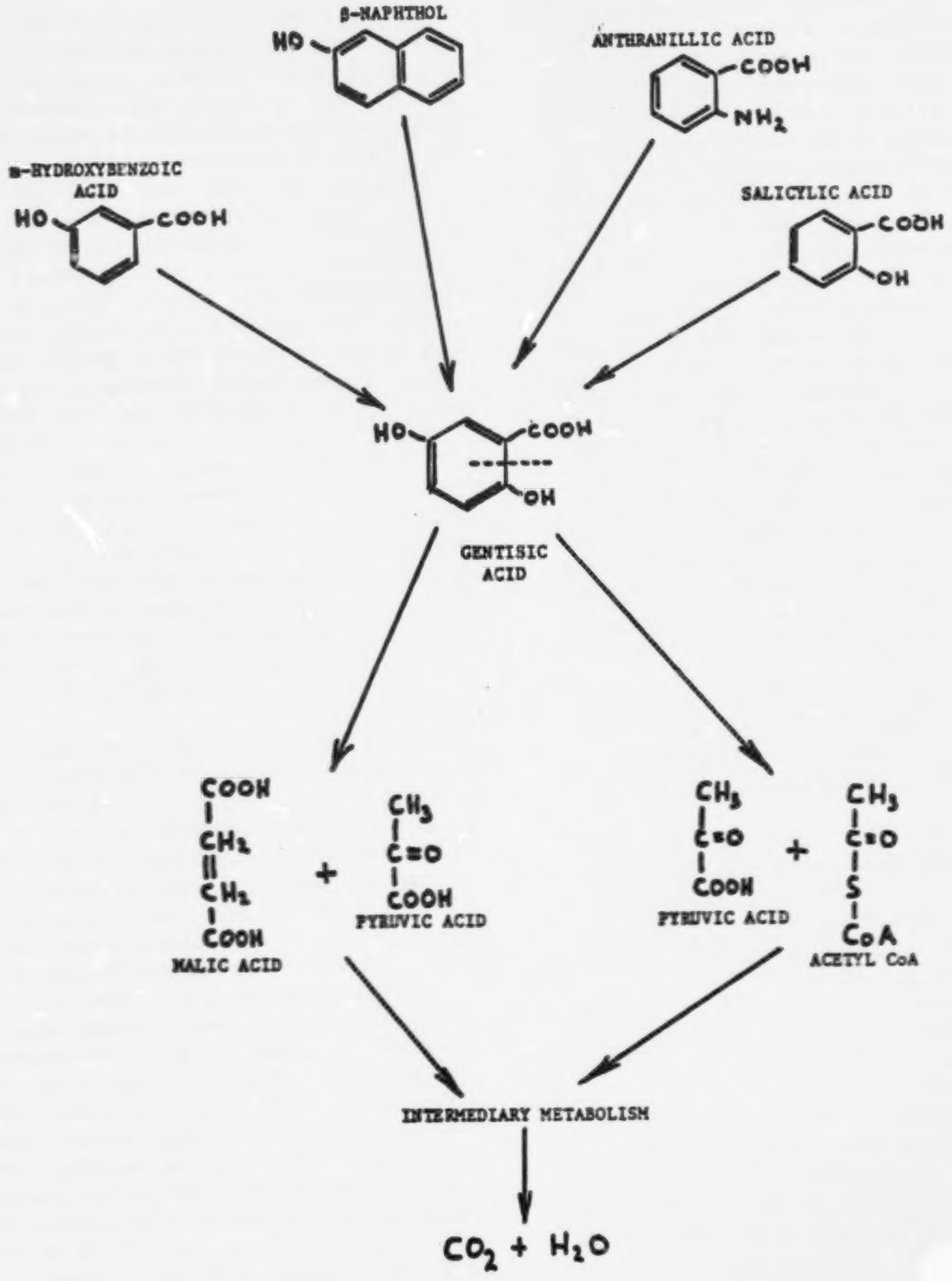
β-NAPHTHOL
HO
ANTHRANILLIC ACID
COOH
NH2
m-HYDROXYBENZOIC ACID
HO
COOH
SALICYLIC ACID
COOH
OH
HO
COOH
OH
GENTISIC ACID
COOH
CH2
CH2
COOH
MALIC ACID
+
CH3
C=O
COOH
PYRUVIC ACID
CH3
C=O
COOH
PYRUVIC ACID
+
CH3
C=O
S
CoA
ACETYL CoA
INTERMEDIARY METABOLISM
CO2 + H2O

Figure 3. Schematic diagram illustrating gentisic acid as a primary ring fission substrate in the microbial metabolism of various aromatic compounds.

cleavage can then occur. Bacteria employ two different modes of enzymatic ring cleavage, known respectively as *ortho* and *meta* fission. Figures 1 and 2 show both types of fission for catechol and protocatechuic acid. *Ortho* fission is the splitting of the bond between the two carbon atoms bearing hydroxyl groups. This results in the formation of dicarboxylic acids. The other pathway, *meta* fission, leads to either an aldehydo-acid or keto-acid by cleavage of a carbon-carbon bond where only one carbon bears a hydroxyl group. Usually, a particular microbial species employs only one method of ring fission for a certain primary substrate. The method of ring fission varies with species, structure of the dihydric phenol, and the substrate upon which the microbial culture has been maintained. This last condition has been demonstrated by Hopper and Taylor (1975)[19] for the cresol isomers. When bacteria were grown on p-cresol, p-cresol was degraded by the *ortho*-fission pathway, but when the same culture had been maintained on m-cresol, p-cresol was degraded via *meta*-fission.

Figure 3 shows the fission pathway for gentisic acid. Fission occurs at the carbon-carbon bond where one carbon bears a hydroxyl group and the other carbon bears the carboxyl substituent.

The trihydric ring fission substrate 1, 2, 4-trihydroxybenzene, found in the degradation of resorcinol, undergoes *ortho*-fission (Larway and Evans, 1965)[20] with the ultimate products being acetic and formic acids. Other trihydric phenols undergo *meta*-fission.

The ultimate ring fission products of most phenolics undergo either fatty acid metabolism or enter the tricarboxylic acid cycle of the microorganisms.

As indicated above, these metabolic pathway studies were carried out with pure cultures of microorganisms under controlled laboratory conditions. For the most part, these studies were conducted in order to discover the enzymes and mechanisms by which microorganisms metabolize aromatic compounds for energy and growth. While pure culture work is important for a basic understanding of biodegradation, it is necessary in relation to biological treatment of wastewaters containing these compounds, to focus attention on mixed microbial communities, such as soil, sewage, and activated sludge. Another concern that is usually not considered in metabolic pathway studies is the rate at which the substrate is metabolized.

Much of the data that exist on the biodegradability of phenolics in mixed cultures in wastewaters is based on oxygen uptake measurements. Early determinations of biodegradability were done by means of the standard biochemical oxygen demand (BOD) test. A summary of this type of data for a large number of pure organic compounds included many phenols (Heukelekian and Rand, 1955).[21] The majority of the studies were done with unacclimated sewage as seed. Under these conditions, the data revealed that phenol, at concentrations below 500 mg/l, was readily degraded. *Ortho*- and *meta*-cresol were degraded at approximately the same rate as phenol, as were α- and β-naphthol. *Para*-cresol and 3, 4-xylenol gave somewhat lower oxygen demands and the BOD's of hydroquinone and 3, 5-xylenol were only one-half that of phenol after five days.

Respirometric studies with acclimated activated sludge demonstrate the behavior of compounds of similar chemical structure, and the ability of microorganisms adapted to a given substrate to oxidize related compounds. The data of McKinney, Tomlinson, and Wilcox (1956)[22] show that organisms acclimated to phenol, o-cresol or m-cresol metabolized phenol, the three cresol isomers, benzoic acid and p-hydroxybenzoic acid to approximately 33 percent of their theoretical oxygen demand (ThOD) in 12 hours. However, the phenol-acclimated sludge oxidized catechol to only 13 percent of its ThOD, while the o-cresol and m-cresol-acclimated sludges metabolized catechol to the same extent as the other compounds (33 percent of ThOD). In the phenol-acclimated system, cresols were oxidized to about the same extent as phenol. The 3, 4- and 2, 4- and 2, 6- and 3, 5-methyl substituted phenols showed progressively less oxidation than phenol, indicating the importance of substituent position on the ring.

These results were later verified in a major study of the decomposition of phenolic com-

TABLE 14

OXIDATION AND REMOVAL OF VARIOUS PHENOLIC COMPOUNDS BY PHENOL-ACCLIMATED BACTERIA. (AFTER TABAK ET AL. (1964.[23])

Test compound	Test concn		Amt of O_2 consumed* (endogenous corrected)
	Initial ppm	Loss ppm	
			μliters
Phenol	100	99	319
Phenol	80	79	252
Phenol	60	59	186
Catechol	100	97	255
Resorcinol	100	98	252
Quinol	100	86	149
Phloroglucinol	60	3	12
m-Chlorophenol	100	50	66
p-Chlorophenol	100	66	80
2,4-Dichlorophenol	60	18	46
2,6-Dichlorophenol	100	35	39
2,4,6-Trichlorophenol	100	70	56
o-Cresol	100	97	417
m-Cresol	100	97	457
p-Cresol	100	97	306
2,6-Dimethylphenol	100	69	40
3,5-Dimethylphenol	100	37	70
2,4-Dimethylphenol	100	81	126
3,4-Dimethylphenol	100	90	189
Orcinol	100	36	72
Thymol	100	44	48
6-Chloro-*m*-cresol	80	51	81
6-Chloro-2-methylphenol	80	37	66
4-Chloro-2-methylphenol	80	50	90
4-Chloro-3-methylphenol	60	46	113
o-Nitrophenol	100	49	48
m-Nitrophenol	100	39	65
p-Nitrophenol	100	32	54
2,4-Dinitrophenol	60	19	66
2,6-Dinitrophenol	60	8	51
2,4,6-Trinitrophenol	100	28	22
4,6-Dinitro-*o*-cresol	100	60	31
2,4,6-Trinitroresorcinol	60	13	6
2,4,6-Trinitro-*m*-cresol	60	8	14
4-Chloro-2-nitrophenol	100	64	123
2-Chloro-4-nitrophenol	60	7	51
2,6-Dichloro-4-nitrophenol	100	9	35
m-Dinitrobenzene	100	25	42
p-Dinitrobenzene	100	20	32
m-Nitroaniline	100	31	70
2,4-Dinitroaniline	100	39	53
m-Nitrobenzaldehyde	100	27	38
3,5-Dinitrobenzoic acid	100	13	48

* Based on 180 min results

pounds by phenol-adapted bacteria (Tabak, Chambers, and Kabler, 1964).[23] In addition to respiration measurements, chemical analysis for residual substrate was also performed. Some of the results of the study are presented in Table 14 and Figures 4 and 5. The data indicate that phenol itself is immediately and rapidly degraded and that dihydric phenols are oxidized to the same extent as phenol. The presence of more than two hydroxyl groups on the ring (e.g., phloroglucinol) increases resistance to degradation. The addition of one methyl group (cresols) appeared to stimulate total oxygen uptake for *ortho-* and *meta-*cresol. Total oxygen uptake for p-cresol was the same as that for phenol although there was a rapid initial uptake. Again, the effect of position of substitution on the ring was illustrated by the dimethylphenols. Nitro-, chloro-substituted, and trihydric phenols were relatively resistant to oxidation.

Summary of Biodegradability Review

As indicated in the above discussion, there is a significant body of literature available concerning the microbial degradation of phenols, especially in pure cultures of microorganisms and in single-substrate systems. This is especially true for both mono- and dihydric-phenols. Less information is available, however, with regard to the biodegradability of the more highly substituted phenols, or of the other complex aromatic constituents of coal conversion wastewaters, such as the mono- and polycyclic nitrogen-containing aromatics, the oxygen- and sulfur-containing heterocyclics, and the polynuclear aromatic hydrocarbons. Furthermore, little information is

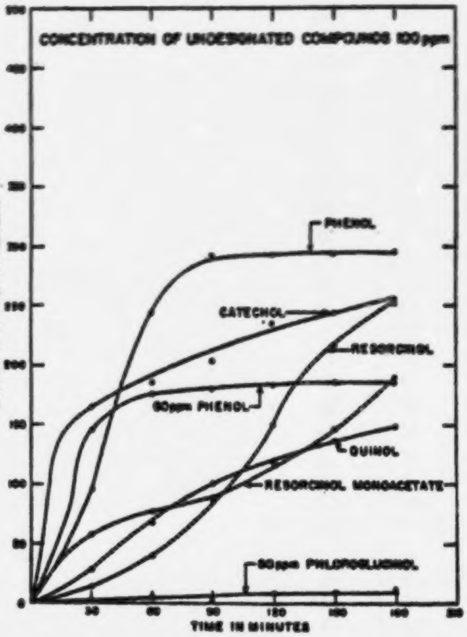

Figure 4. Oxidation of dihydric phenols. (From Tabak et al (1964.[23])

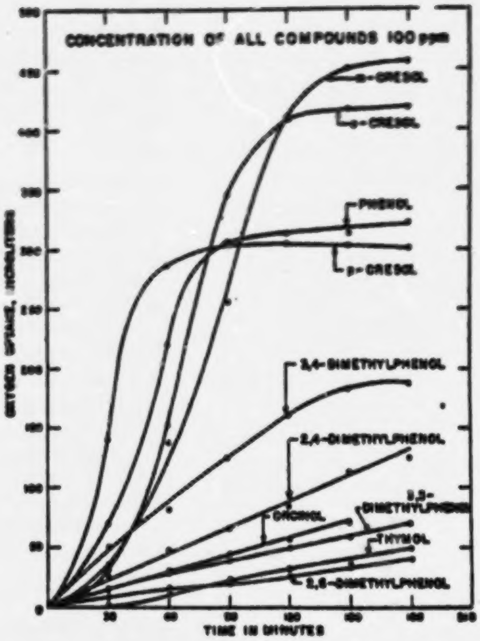

Figure 5. Oxidation of cresols and other methylphenol derivatives. (From Takak et al. (1964.[23])

available regarding the biodegradation of specific phenolic compounds in complex mixtures such as those characteristic of coal conversion wastewaters. Additionally, considering the needs from a wastewater treatment viewpoint, there is also little information available regarding the rate at which these compounds are microbially degraded in mixed cultures, and the concentrations at which these compounds become inhibitory to microbial degradation.

CONCLUSIONS

An attempt has been made to determine the chemical characteristics of byproduct wastewaters from coal gasification and coal liquefaction processes. Approximately 60-80 percent of the total organic carbon appears to be phenolic in nature, consisting of monohydric, dihydric, and polyphenols. The remainder of the organic material consists of mono- and polycyclic nitrogen-containing aromatics, oxygen- and sulfur-containing heterocyclics, polynuclear aromatic hydrocarbons, and simple aliphatic acids. The composition of the wastewaters appear to be relatively uniform, especially with respect to the phenolic constituents, regardless of the specific process technology and type of feed coal employed. At the concentrations reported, the discharge of these wastewaters would have an adverse impact on aquatic life and, as a result, a significant degree of wastewater treatment is necessary. While aerobic biological processes appear to be among the methods of choice for treating these wastewaters, the following types of information are required in order to assess the biological treatability of these coal conversion wastewaters and to develop suitable design and operating guidelines: (a) an assessment of the biodegradability of the constituent compounds, as reviewed above; (b) biokinetic information describing the rate at which degradation of the constituents takes place; (c) the concentration levels at which microbial degradation of the constituents is inhibited; and (d) how the constituents will behave in a composite mixture representative of coal conversion wastewaters. In view of the paucity of information available regarding the microbial degradation of many of the constituents identified in coal conversion wastewaters, an experimental program to provide such information is underway.

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BIOLOGICAL TREATMENT OF COAL CONVERSION CONDENSATES

Irvine W. Wei[†] and D. J. Goldstein
Water Purification Associates
238 Main Street
Cambridge, Massachusetts 02142

Abstract

Biochemical oxidation is an important way to remove organic contamination from foul condensates in coal conversion plants. The design considerations are discussed; oxygen is recommended in preference to air, and a test with mutated bacteria is recommended. Reactor configurations are also discussed. When the organic contamination is high, the use of oxygen requires forced cooling and a combined cooling tower/trickling filter is suggested for the test. Preliminary plant designs are given for two situations in a Hygas plant: one when lignite is fed and one when a bituminous coal is fed.

Waters that condense and are removed from a coal conversion plant will often be highly contaminated with organic matter. The level of contamination depends on the process and on the coal. Condensate from Solvent Refined Coal, Synthoil, or H-Coal can be expected to be very dirty. From gas plants the contamination seems to be higher from a lower temperature and a shorter residence time. Thus Lurgi and probably Synthane will give quite dirty water, Hygas will give less dirty water, and Bigas the least dirty. The coal rank is very important. Condensate from a Hygas plant fed lignite is many times more contaminated than condensate from the same plant fed a bituminous coal.

Dirty condensate will have to be treated for reuse. Reuse possibilities include makeup to a wet flue gas desulfurization system, use for dust control, and makeup to a cooling tower. The first in line of the commonly assumed treatments is solvent extraction. If the extractable concentration is high enough that its value as a fuel or as crude phenol can partially offset cost, then solvent extraction, or a treatment accomplishing the same result, should be used. For lower levels of contamination solvent extraction will probably not be economically justifiable. Most condensates will next have to be treated to remove ammonia and many will require removal of hydrogen sulfide. After ammonia separation the next treatment in series will often be biological oxidation. The contamination in many waters seems to be biodegradable. Phenol, a common, high level contaminant, is biodegradable.

It is the purpose of this paper to put forward preliminary designs for biological oxidation plants for these waters. Biological oxidation and solvent extraction are both treatments to accomplish the same objective, to remove organic contamination. They are not mutually exclusive. If solvent extraction is not economic and is not used, biological treatment will usually be required. But if solvent extraction is used its cost is quite dependent on the level of contamination acceptable in its effluent and it may pay to follow solvent extraction with biological oxidation. When treated condensate is to be used as makeup to a cooling tower, biological treatment has some disadvantages. Phosphorus will have to be added and will not be all used up in the treatment. Dissolved CO_2 and suspended solids are increased by biological treatment. Possibly residual ammonia, which is necessary as a nutrient in biological treatment, will be higher than need be left after ammonia stripping. We are not, at the moment, able to say whether biological treatment should be reserved for situations where solvent extraction is not used, or whether biological treatment will be useful subsequent to solvent extraction.

DESIGN CONSIDERATIONS

Major design considerations for biochemical oxidation include:

A. Reactants
    a. Phenols and other organics
    b. Other required nutrients
    c. Oxidants
B. Biological Agents
C. Reactor Configurations

[†] Irvine W. Wei is also Assistant Professor of Civil Engineering, Northeastern University, Boston, Massachusetts 02115.

A. Reactants

During biological treatment the organic constituents of wastewaters, such as phenols, are oxidized and utilized as the sources of carbon and/or energy while the reaction is mediated by biological agents. Phenol is usually considered biodegradable. However, if the phenol concentration exceeds a certain threshold level, phenol itself can inhibit the bio-oxidation. This threshold concentration of phenol has been reported to be 500 mg/l[1] and 1,000 mg/l;[2] these concentrations are unlikely to be exceeded in the completely mixed bioreactor of an activated sludge system. Should the phenol concentration become inhibitory, a proper scheme of dilution may be needed. Dilution can be achieved by internal recirculation of treated water or by adding an external dilutant.

Other organics, particularly those refractory in nature, may significantly affect the performance of biological treatment and consequently the dilution requirement. Although this category of organics may be measured by the difference between COD and BOD, its effect on bio-oxidation appears to be poorly understood and requires pilot testing with the specific wastewater to be treated.

To satisfy nutritional requirements of the biological agents responsible for bio-oxidation, certain inorganic macro and micro nutrients may have to be provided. Macro nutrients such as nitrogen and phosphorus are required in proportion to phenol content. A typical weight ratio as used at Bethlehem Coke Plant[3] is phenol:N:P = 70:5:1. Excess N is available in the condensates, so the ammonia concentration will be reduced to the required nutritional level by proper ammonia recovery prior to biological treatment. Phosphorus will have to be supplied by adding phosphoric acid or equivalent. Various trace nutrients such as manganese, copper, zinc, and other metals might not be available in the wastewater but are required by biological agents.[4]

For the ultimate oxidant for bio-oxidation, molecular oxygen is the most common choice, whether it comes from compressed air or high-purity oxygen gas. The use of high purity oxygen rather than air has gained increasing acceptance in aerobic biological treatment. In addition to certain advantages in treatment performance,[5] it has been reported that the use of high purity oxygen appears to be more energy-effective in the transfer of oxygen.[6] The total energy required to separate oxygen from air, and then dissolve the oxygen in water, is less than the energy required to dissolve directly in water the same amount of oxygen from air.[6] Othmer[6] reported that normal aeration under 1 atmosphere required about 0.5 kW-hr of energy to dissolve 1 pound of oxygen from air, whereas this requirement dropped to less than 0.05 kW-hr to dissolve 1 pound of commercial oxygen. For the high purity oxygen activated sludge plant designs given later, the energy for dissolution is 0.09 kW-hr/lb O_2. For oxygen production the energy is about 0.165 kW-hr/lb O_2,[11] totaling about 0.26 kW-hr/lb O_2. Furthermore, since oxygen is required and produced in many coal conversion plants, it can be made available for biological treatment at the cheapest possible price. Approximately 3,000 tons per day of oxygen will be needed in a standard size SNG plant, and the amount of oxygen required for the high purity oxygen activated sludge (HPOAS) system may be about 10 percent or less of that required for coal conversion, depending on the amount of BOD to be removed in the biological treatment.

B. Biological Agents

The use of specially prepared bacteria for more effective biological treatment of certain industrial wastes has been recently publicized.[7] These bacteria are prepared from the parent strain through induced mutation, which may involve exposing the parent strain to programmed radiation, and subsequently through proper enrichment allowing for the buildup of a large population of mutant bacteria. The mutant baceria so produced are far more efficent in degrading certain pollutants than the parent strains occurring in nature or the mixed culture commonly used in activated sludge process. For instance, the mutated *Pseudomonas sp.*, commercially marketed as PHENOBAC, could increase the rate of degradation by about twofold. When parent strains and mutant strains were exposed to 500 mg/l of phenol in a laboratory test, the time for 100 percent degradation (as measured by ring disruption) was 25 hours and 8 hours respectively.[8]

In another laboratory study simulating the treatment of aqueous effluents (using a synthetic solution of phenol with other additives) from coal conversion processes,[2] the acclimated activated sludge from the Bethlehem Coke Plant and PHENOBAC were used as the biological agents. In terms of phenol degradation, the efficiency of the mutated bacteria was noted to be about two times that of the acclimated sludge.[9] It was also found convenient to handle the predried and packaged mutant bacteria which could be reactivated by immersion in 100° F water for about an hour.[2,7] The cost of PHENOBAC, which comes in 25-100-lb. packages, is about $16 per pound.

In addition to the laboratory tests reported above, mutant bacteria have also been found useful in certain full-scale High Purity Oxygen Activated Sludge (HPOAS) facilities. In the treatment of a number of petrochemical and refinery wastewaters, the performance of PHENOBAC was compared in parallel with that of ordinary activated sludge, and PHENOBAC was found to achieve:[10]

1. better process stability;
2. enhanced removal of TOC; and
3. reduction of foaming in bioreactors and liquid-solids separators.

In view of the above information available from various independent sources, the use of mutant bacteria warrants serious consideration in the future pilot facilities treating coal conversion wastes. A side-by-side comparison on the performance of mutant bacteria, acclimated sludge, and ordinary activated sludge would be highly desirable.

C. *Reactor Configurations*

The most common configurations of bioreactors include: trickling filters, where fixed biological growth is maintained, and activated sludge systems, where suspended growth is utilized. In general, trickling filters have been used for their simplicity and low cost of operation, resilience to shock loads and toxic substances, while activated sludge has been known for its high treatment efficiency, better control and reliability.

It is not a new idea to combine the desirable attributes of trickling filter and activated sludge processes into the most cost-effective system by use of dual biological processes (using a combination of trickling filter and activated sludge) for industrial wastewater treatment.[12] Success in the treatment of wastewaters form organic chemical manufacturing, petrochemical refining, and meat processing industries has been reported.[12,13] In most of the reported cases, the water contaminants of primary concern have been phenols and BOD.

Since the use of HPOAS (high purity oxygen activated sludge) appears to have significant advantages at coal conversion plants, it is essential to consider the control of water temperature in the covered bioreactors. Oxidation of hydrocarbons are exothermic reactions. The oxidation of C, CH, and CH_2 can theoretically lead to 1° F temperature rise per 184, 170, and 161 mg/l BOD removed, assuming 100 percent biodegradability. For phenol, this temperature rise will be about 1° F per 165 mg/l BOD removed. Therefore, considering the various heat losses in the bioreactors, it may be reasonably assumed that the removal of 200 mg/l BOD will cause an increase in water temperature of 1° F.

Biological agents are known to be temperature sensitive. It has been recommended[14] that the water temperature in the aerobic biological treatment of coke plant wastes be 95-100° F throughout the year. Consequently, when a high level of BOD removal is to be achieved by HPOAS, the temperature rise may become excessive and a means of cooling may become necessary.

To take the advantages of dual biological treatment processes and to satisfy the cooling requirement, we suggest merging a trickling filter with a cooling tower as an integral unit when HPOAS is used. In the treatment of refining wastes it has for more than two decades been found economical and desirable to achieve bio-oxidation and water cooling in a cooling tower structure.[15] Functionally, the cooling tower in this case is analogous to the trickling filter in terms of organic removal. Whether this unit should be designed as a trickling filter or a cooling tower depends on which function will be limiting.

EXEMPLARY WASTEWATER CHARACTERISTICS

Two examples will be used in the following design studies, based on Hygas plants using a lignite and a bituminous coal feed. Details are given on Table 1.

ALTERNATIVE PROCESS TRAINS

1. Air Activated Sludge

The air activated sludge (AAS) system is probably the most common treatment system used for wastewaters with constituents similar to coal conversion wastewaters, e.g., coke plant wastes. An extensive literature review on the biological oxidation of coke plant wastes was reported by Barker and Thompson[18] in 1973. Among the treatment systems discussed, AAS is the predominant treatment system of success. Laboratory studies[27] abroad have also indicated that AAS systems can satisfactorily treat the coal conversion wastes with the following characteristics:

Total ammonia	~ 1,500 ppm
Total phenols	~ 300 ppm
Thiocyanate	~ 150 ppm
Chloride	~ 2,500 ppm

Among the full-scale AAS facilities treating coke plant wastes, the one at Bethlehem Coke Plant, Bethlehem, Pennsylvania, has been in operation since 1962, and seems to have the most complete data available in the literature.[3] Since there has been no pilot tests for the treatment of coal conversion wastes by AAS in the United States, we begin by basing a preliminary design on the data available from the Bethlehem AAS system and essentially scale up from this existing treatment facility.

The scaled design is based on the assumption that the biodegradability of coal conversion wastewaters is identical with that of the coke wastewater. This assumption is open to question. No data on COD of the coke wastewater is available in Reference 3. However, an analysis of an average coke plant waste indicated that the theoretical oxygen demand due to phenols, which are readily biodegradable, constitute about 68 percent of the measured COD while for coal conversion

TABLE 1

WATER ANALYSES AND FLOWS FROM TWO HYGAS PLANTS

	Lignite feed	Bituminous coal feed
BOD$_5$ (mg/l)	13,000 - 18,000	2,000 - 3,000
COD (mg/l)	25,000 - 30,000	~ 3,000
Phenol as C_6H_5OH (mg/l)	3,000 - 5,000	300 - 500
NH_3 as N (mg/l)	~ 290	~ 30
Flow, 10^3 lb/hr	295	535
10^6 gals/day	0.85	1.5
m^3/sec	0.037	0.066

Analysis from References 5 and 16. Ammonia is reduced to the listed level by prior treatment. Flow for the lignite feed from Reference 5 and for the bituminous feed from Reference 17.

wastewater phenol averaged about 40 percent of the COD.[19] Although the question of biodegradability can only be fully answered by pilot testing, the above comparison indicates certain differences in chemical composition between coke plant and coal conversion wastewaters. It is essentially unknown at this point whether and how this will affect the design of biological treatment. Should the assumption of biodegradability become invalid to any extent, there would be corresponding limitation on the usefulness of the preliminary design.

One of the most important design considerations regarding biological treatment of coke plant wastes is to determine if the waste contains any inhibitory constituents which may render the biological treatment system totally or partially unfunctional. If these constituents exist, it is essential to determine their threshold concentrations and thus the dilution required for the influent to the biological treatment system. Some inhibitory constituents and their threshold concentrations found in our literature search include:

Phenol = 500[1] - 1,000[2] mg/l
Ammonia = 1,200[18] - 2,000[3] mg/l
Chloride = 2,000[18] mg/l

Phenol will normally be kept at a low enough level in the mixed reactor. Ammonia will have to be reduced by prior treatment. Chloride will not usually reach toxic level.

The following rules were used to produce the scaled design. Most numerical values came directly from the Bethlehem AAS experience[3] while the four biokinetic coefficients, k, K_s, Y, and k_d were evaluated by us on the basis of data from Reference 3.

Nutrients such as nitrogen and phosphorus are essential for biological treatment. The required weight ratio is assumed to be invariant and is phenol:N:P = 70:5:1. Excess N is available in the wastewater, and the ammonia nitrogen concentration will be reduced to the proper level by ammonia recovery prior to biological treatment. Phosphorus will have to be supplied by adding phosphoric acid or equivalent.

The design of bioreactors was based on a biokinetic model developed by Lawrence and McCarty.[20] This model is based on an empirically developed relationship between the rate of growth of microorganisms and the rate of consumption of degradable contaminants. Degradable contaminants are called "substrate" as they are "food" for the microorganisms. The relationship is

$$\frac{dX}{dt} = Y\frac{dS}{dt} - k_dX \qquad (1)$$

where
X = concentration of microorganisms
t = time
Y = growth yield coefficient; weight of microorganisms produced per weight of substrate removed
S = concentration of substrate or degradable contaminant
k_d = microorganism decay coefficient, time^{-1}.

If Eq. (1) is divided by X we obtain

$$\frac{1}{X}\frac{dX}{dt} = \frac{Y}{X}\frac{dS}{dt} - k_d \qquad (2)$$

In Eq. (2) each term has the dimension (time^{-1}) and compatible units must be used. The left hand side of Eq. (2), which is the rate of increase of concentration of microorganisms per unit concentration, may also be written $1/\Theta_c$, where Θ_c is called the mean cell residence time or sludge age. The first term on the right hand side of Eq. (2) includes the quantity $\frac{1}{X}\frac{dS}{dt}$ which is the rate of decrease of concentration of substrate per unit concentration of microorganisms. This quantity is a function of the concentration of substrate and the Lawrence and McCarty model assumes the function

$$\frac{1}{X}\frac{dS}{dt} = \frac{k_sS}{K_s} \qquad (3)$$

In sum, the model can be written

$$\frac{1}{\theta_c} = \frac{YkS_1}{K_s + S_1} - k_d \qquad (4)$$

The rest of the major design equations are:

$$XV = \frac{YQ\theta_c(S_0 - S_1)}{1 + k_d\theta_c} \qquad (5)$$

$$r = \frac{q}{Q} = \frac{1 - (V/Q)/\theta_c}{(X_r/X) - 1} \qquad (6)$$

$$P_x = \frac{XV}{\theta_c} \qquad (7)$$

$$w = \frac{P_x}{X_r} \qquad (8)$$

The meaning of all symbols used is shown in the schematic flow diagram in Figure 1. The four basic coefficients were evaluated from information given in Reference 3. In this reference are tabulated experimental values of (lb phenol removed)/(lb microorganisms)(day), which is $\frac{1}{X}\frac{dS}{dt}$, as a function of the phenol concentration, S. These values are plotted in Figure 2 and the curve so obtained is fitted to Eq. (3) by noting that k is the value of $\frac{1}{X}\frac{dS}{dt}$ when S is large and K_s is the value of S when $\frac{1}{X}\frac{dS}{dt} = k/2$. Also from Reference 3 the $\frac{1}{X}\frac{dX}{dt}$ can be calculated. On Figure 3 is plotted $\frac{1}{X}\frac{dX}{dt}$ against $\frac{1}{X}\frac{dS}{dt}$ from which the coefficients Y and k_d are determined.

The values of the coefficients determined in this way are:

k = 0.9 lb C_6H_5OH/lb MLSS•day = 2.14 lb BOD/lb MLSS•day
K_s = 0.17 mg/l C_6H_5OH = 0.4 mg/l BOD
Y = 0.4 lb sludge/lb C_6H_5OH processed = 0.17 lb sludge/lb BOD processed
k_d = 0.17 $(\text{day})^{-1}$

These coefficients were evaluated in terms of phenol removal and then converted to BOD based on the theoretical oxygen demand of 2.38 units per unit of phenol.

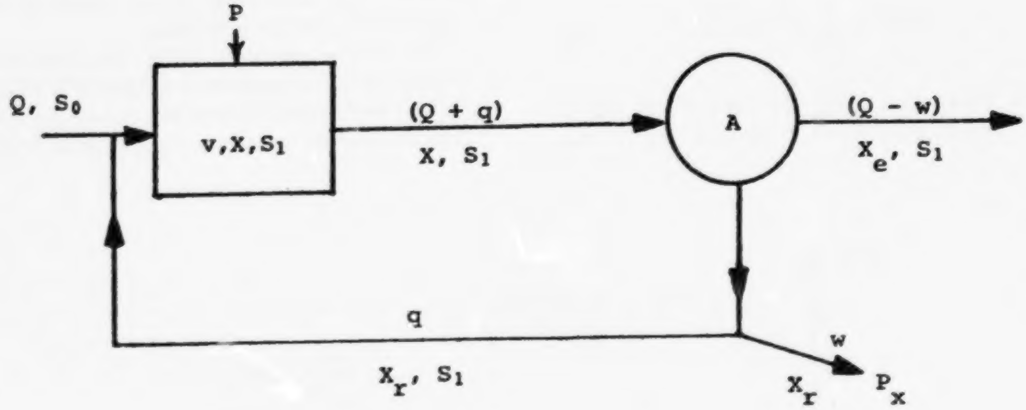
The aerator power requirement is taken to be proportional to the BOD or phenol removed. At Bethlehem Coke Plant the power requirement is based on 18.2 lb phenol removed/(day)(hp) or 43.3 lb BOD/(day)(hp), which compares closely with typical values in the literature of 45-50 lb BOD removed/(day)(hp).[21]

The best way to size the clarifier is to determine experimentally the relationship between initial settling velocity and suspended solids concentration.[22,23] This typically takes the form shown in Figure 4.[24] The aeration vessel volume and solids separator volume can then be determined for series of concentrations of microorganisms, X, and the optimum concentration of microorganisms determined. We have no data to plot Figure 4 and have, therefore, used the one available point from Reference 3, namely X = 2,600 mg/l and the clarifier overflow rate is 685 gal/(day)(ft^2). For use in Eq. (6) we also assumed the same value of $X_r/X = 3.44$. The value of X_r/X is a function of the performance of the solids separator.

Subsequent treatment of waste sludge depends on the means of ultimate disposal and the method of transport to the disposal site. Sludge is beneficial when added to coal ash and this seems to be an attractive means of ultimate disposal as the nutrient content of waste sludge will be conducive to the revegetation process. The sludge may be transported by tank truck or pipeline, and the final selection is dictated by the economics of these operations. The method of transport will in turn determine whether any sludge treatment is desirable. The objective of sludge treatment in our designs is primarily volume reduction. For assumed transportation by tank truck, dissolved air flotation (DAF) thickening followed by vacuum filtration is included. These sludge treatment processes are sized according to the following criteria: 20 lbs dry solids per square foot per day for the DAF thickener, and 120 lbs dry solids per square foot per day for vacuum filters. These values are assumed,[25] not scaled, because Bethlehem Coke Plant discharges its sludge to a sewage plant and provides no sludge treatment.

The results of the calculations for the two exemplary waste waters described on Table 1 are given on Table 2. For each water calculations are presented for a two-stage process with 95 percent removal in each stage and an equivalent single stage process with 99.75 percent removal. The volumes are insignificantly different, showing that the reaction is zero order in the range of concentrations of BOD of interest. Complete calculations are, therefore, presented for 95 percent and 99.75 percent removal, in single stages, for each water. The results for the lignite at 99.75 percent removal are also shown in Figure 5.

Some preliminary comments can be made. The clarifier diameters are small and with very little increased investment larger diameters can be used and the somewhat high overflow rate



Q = flow rate of liquid waste to be treated biologically, volume/time;

q = flow rate of recycled sludge, volume/time;

w = flow rate of wasted sludge, volume/time;

S_0 = influent substrate concentration, mass/volume;

S_1 = effluent substrate concentration, mass/volume;

X = microbial mass concentration, mass/volume;

X_e = microbial mass concentration in the clarified overflow from the solids separator, mass/volume;

X_r = microbial mass concentration in the underflow from the solids separator, mass/volume;

P = power requirement for aeration, energy/time;

P_x = excess microorganisms production rate, mass/time.

Figure 1. Air activated sludge model.

assumed can be reduced. The hydraulic residence times listed are not unreasonable. The quantity called F/M on Table 2 is $\frac{1}{X}\frac{dS}{dt}$ in Eq. (2) and is calculated from the equation

$$F/M = \left(\frac{1}{\theta_c} + k_d\right)/Y \qquad (9)$$

The listed quantities are very much higher than usual practice. It should be noted, however, that the BOD of phenols has been calculated as 2.38 times of phenol concentration, i.e. we have assumed BOD to be equivalent to the theoretical oxygen demand of phenol. The calculated F/M in terms of BOD may thus be on the high side.

The major problem with the biokinetics limited design presented on Table 2 is the high rate of BOD removal and the consequent high rate of oxygen transfer required. In all designs

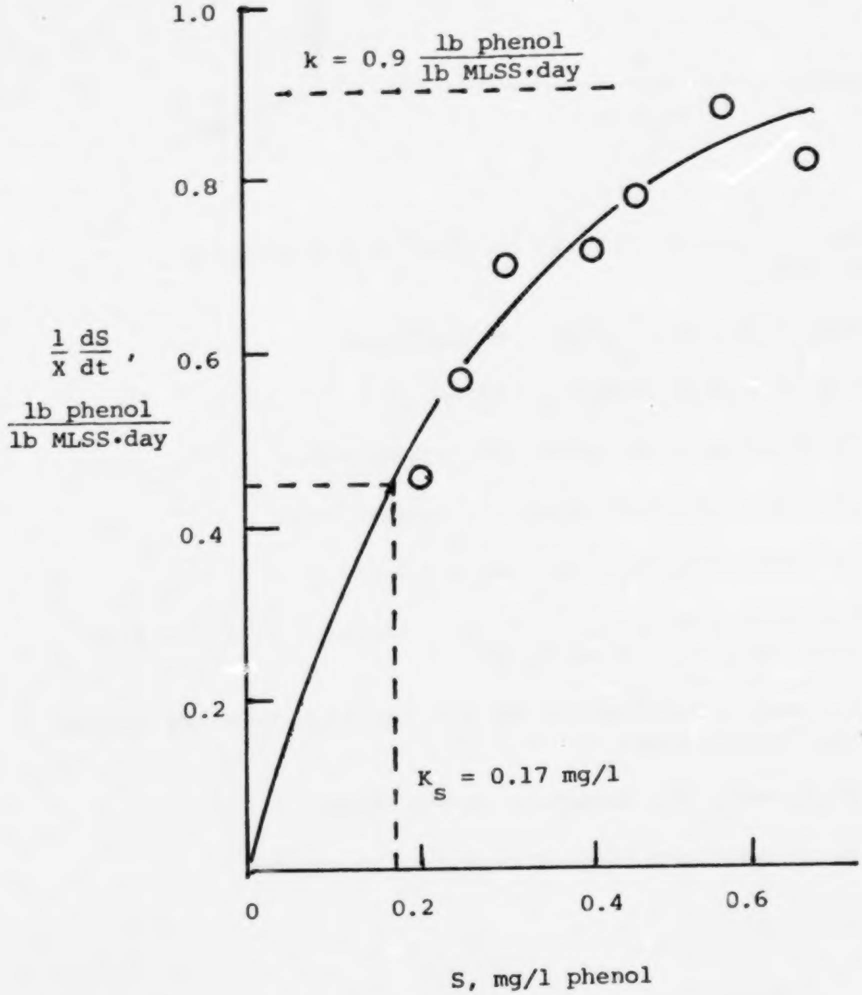


Figure 2. Substrate utilization vs. substrate concentration (based on data from Ref. 3).

this exceeds 200 mg/(l)(hr). Suppose, first, that surface aerators are used and that the aeration basins are made 15 ft deep. The horsepower for the aerators is found to be applied at a rate of about 120 hp/10^3ft^2. If power were to be applied at this rate the energy to transfer each pound of oxygen would probably increase unacceptably. Potential remedial measures include: (1) use of shallower basins, such as a basin depth of 9 feet instead of 15 feet, this will lead to an energy application of less than 75 hp/10^3ft^2; (2) use of oxygenation systems which are more efficient than surface aerators, such as submerged aerators or using high purity oxygen rather than ordinary air as the source of oxygen.

2. High Purity Oxygen Activated Sludge (HPOAS)

As discussed previously HPOAS has the advantages of energy effectiveness and the ready availability of high purity oxygen at most coal conversion facilities. The following preliminary HPOAS design for lignite feed is based on the information supplied by Union Carbide Corporation.

No kinetic coefficients were used in the design of HPOAS. Instead, an empirical approach using F/M ratios and MLVSS data based on past experience with similar industrial wastewaters was followed. It is felt that in the treatment of high stength industrial wastewaters the process design may frequent-

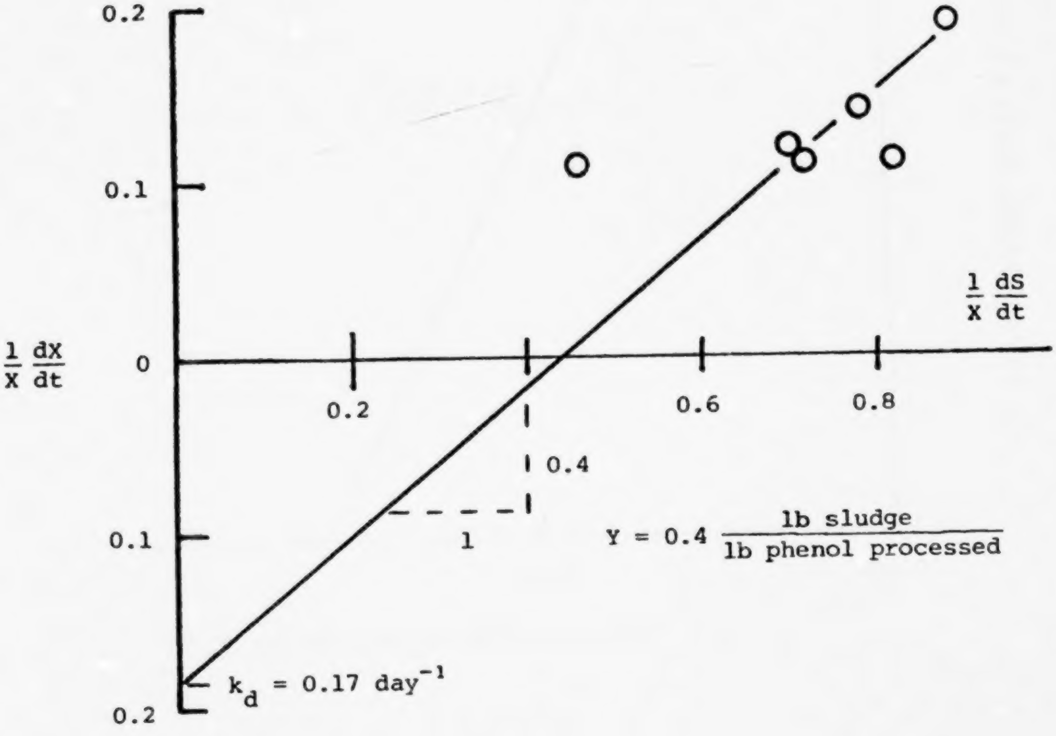


Figure 3. Sludge growth rate vs. substrate utilization rate (based on date from Ref. 3).

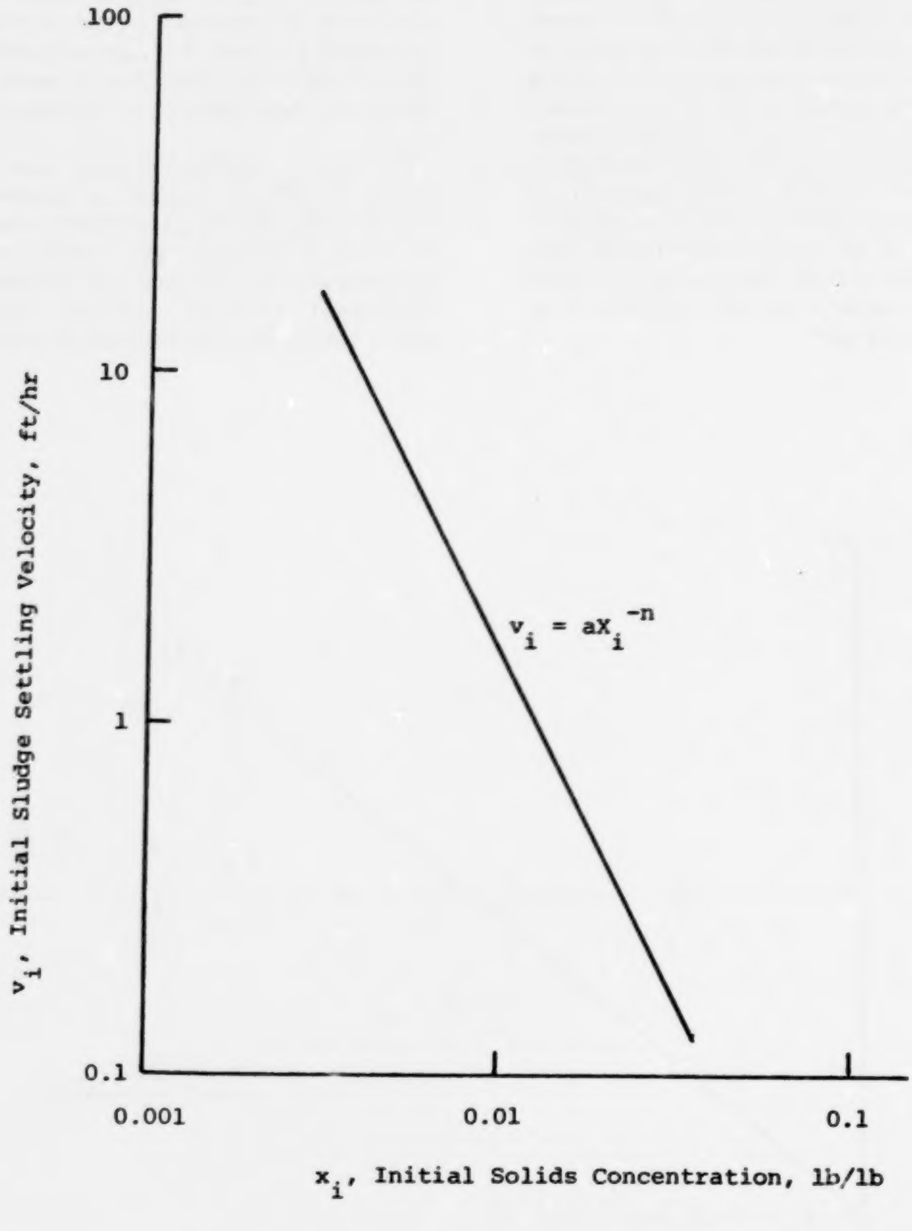


Figure 4. Typical settling velocity vs. solids concentration.

TABLE 2

CALCULATIONS ON AIR ACTIVATED SLUDGE PLANTS

	Lignite Feed			Bituminous Coal Feed		
	First 95%	Second 95%	99.75%	First 95%	Second 95%	99.75%
S_0, mg/l	18,000	900	18,000	3,000	150	3,000
Q, 10^6 gal/day	0.85	0.85	0.85	1.5	1.5	1.5
S_1, mg/l	900	45	45	150	7.5	7.5
θ_c, days	5.16	5.25	5.25	5.19	5.70	5.70
XV, 10^9 (mg)(gal)/l	6.80	0.34	7.20	2.00	0.11	2.21
V, 10^6 gals	2.61	0.13	2.77	0.77	0.04	0.85
Total V, 10^6 gals	2.75			0.81		
r	0.17		0.16	0.37		0.37
q, 10^6 gal/day	0.14		0.13	0.55		0.55
P_x, 10^3 lb/day	11.0		12.6	3.2		3.2
w, 10^6 gal/day	0.15		0.17	0.043		0.043
P, hp	2800		2940	820		860
D, hw	2080		2190	610		640
Clarifier area, ft^2	1240		1240	2190		2190
Clarifier dia., ft	40		40	53		53
DAF thickener, ft^2	550		630	160		160
Vacuum filter, ft^2	96		110	28		28
Residence Time, days	3.1		3.3	0.51		0.54
F/M, $\frac{\text{lb BOD}}{\text{(lb sludge)(day)}}$	2.1		2.1	2.1		2,0

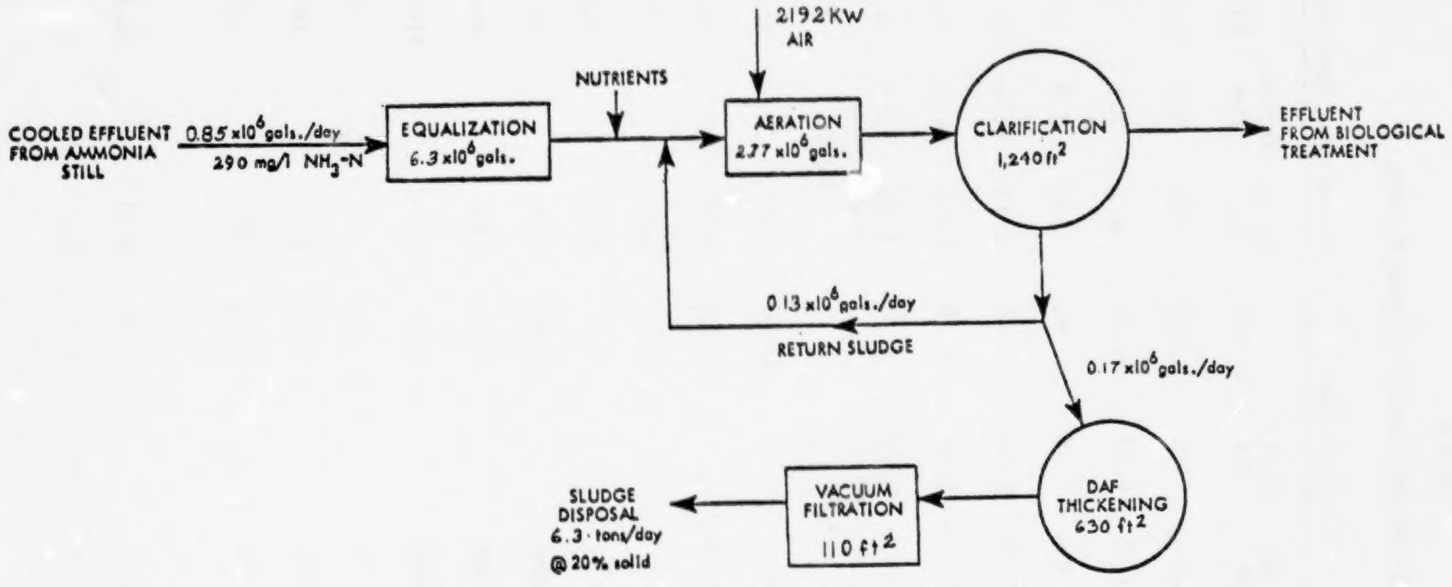

COOLED EFFLUENT FROM AMMONIA STILL
0.85 x10^6 gals./day
290 mg/l NH3-N
EQUALIZATION 6.3 x10^6 gals.
NUTRIENTS
2192 KW AIR
AERATION 2.77 x10^6 gals.
CLARIFICATION 1,240 ft2
EFFLUENT FROM BIOLOGICAL TREATMENT
0.13 x10^6 gals./day
RETURN SLUDGE
0.17 x10^6 gals./day
DAF THICKENING 630 ft2
VACUUM FILTRATION 110 ft2
SLUDGE DISPOSAL 6.3 · tons/day @ 20% solid

Figure 5. Air activated sludge system (AAS) for Hygas plant with lignite feed (from Table 2).

ly be dictated by considerations other than biokinetics, such as oxygen transfer and/or solids separation. However, if biokinetic data can be obtained and compiled properly by using an appropriate reaction model, we should be able to expand our data base and make rational designs easier in the future.

The HPOAS system design consists of multitrains in parallel, with each train consisting of multistages to obtain a quasi-plug flow condition. High purity oxygen is fed to the space above the liquor level in each stage of the oxygenation basin, and oxygen transfer is accomplished by use of surface aerators or equivalent. The dissolved oxygen concentration in the mixed liquor will be maintained at about 5 mg/l rather than 2 to 3 mg/l as commonly used in the AAS system. As with the AAS system, two steps of HPOAS treatment are used with each step achieving about 95 percent removal of BOD.

Two key parameters for the design of activated sludge systems are mean F/M (food to microorganism) ratio and MLVSS (mixed liquor volatile suspended solids). The F/M ratios for step 1 and step 2 differ because of the difference in BOD loading; F/M is 0.8 in step 1 and 0.3 in step 2. The MLVSS will be substantially larger than that for the AAS system because of improved settling velocities of the oxygen sludge, and the MLVSS in this case is assumed to be 7,300 mg/l in step 1 and 4,500 mg/l in step 2. The clarifiers are designed on the basis of an overflow rate of 400 gals/(day)(ft^2) in step 1 and 300 gals/(day)(ft^2) in step 2. These overflow rates are expected to give low suspended solids concentration in the overflow. The design is summarized on Table 3.

The oxygen requirement, pounds of oxygen required per pound of BOD removed, is a function of F/M and COD/BOD ratios.[26] The effect of COD/BOD ratio may be particularly significant in this case as the fate of COD in the biological treatment of coal conversion wastes is unknown at present. The oxygen requirement is assumed to be 1.03 lb/lb BOD removed in step 1 and 1.21 lb/lb BOD removed in step 2. Whenever COD needs to be evaluated in the biological treatment, the removal of COD is assumed to be equal to that of BOD; this assumption is conservative and should lead to a design on the safe side.

The average oxygen utilization in the oxygenation basin depends on the purity of the oxygen in the gaseous mixture which essentially consists of feed oxygen and the carbon dioxide produced as a result of the biochemical oxidation. Therefore the average oxygen utilization percentage will increase as the feed BOD concentration decreases and is assumed to be 79 percent in step 1 and 80 percent in step 2. Based on the oxygen requirement and average oxygen utilization efficiency, the amount of oxygen to be transferred can be calculated.

The energy requirement is estimated as follows. The surface aerators consume about 1 hp-hr for 7.8 lb oxygen supplied, or 0.0956-kW-hr/lb oxygen supplied. Air separation consumes about 0.165 kW-hr/lb oxygen.[11]

A major design consideration is the control of water temperature in the oxygenation basin. As discussed previously, the removal of 200 mg/l BOD will cause an increase in water temperature of 1° F. Since the removal of BOD in step 1 is 95 percent of 18,000 mg/l, this will result in a temperature rise of about 85° F. To maintain the temperature at 95-100° F in the oxygenation basin, it will be necessary to recycle 3.4 x 10^6 gal/day of the mixed liquor at a temperature of about 97° F and to reduce its temperature to 80° F in a cooling tower, as shown in Figure 6. The temperature of the 0.85 x 10^6 gal/day feed is assumed maintained at 80° F from the equalization basin. The broken line in Figure 6 shows the recycling of the clarified water through the cooling tower for more flexible operation.

3. *Activated Trickling Filter-High Purity Oxygen Activated Sludge (ATF-HPOAS)*

In Figure 6, showing the HPOAS system, the cooling would usually be accomplished by passing the return flow through coils situated in a spray tower. Water from the clarifier overflow can be sprayed onto the outside of the coils and a forced air draft used to evaporate some of the water and so cool the return flow. It would be convenient to simply spray the return flow itself into the spray cooling tower, achieving

TABLE 3

DESIGN OF THE HPOAS SYSTEM[a]

Design Basis	
Flow, 10^6 gal/day	0.85
BOD_5, lbs/day	127,600
BOD_5, mg/l	18,000
COD, mg/l	28,000
COD/BOD_5	1.56
Wastewater temperature, °F	80°F
pH	Adjusted as required
Nutrients	Phosphorus to be added

System Design	Step 1	Step 2
Flow, Q (10^6 gal/day)	0.85	0.85
Retention time, hrs (based on feed flow)	74	16
MLSS, mg/l	7,800	5,100
MLVSS, mg/l	7,300	4,500
Sludge Recycle Rate, %Q	35	35
Mean biomass loading, lbs BOD_5/(lb MLVSS)(day)	0.8	0.3
Volumetric organic loading, lbs $BOD_5/(10^3 ft^3)$(day)	364	84
Average D.O. level, mg/l	5.0	5.0
Oxygen supplied, tons/day	79.0	4.6
Average oxygen utilization efficiency, %	79	80
Secondary clarifier overflow rate, gal/(day)(ft^2)	400	300
Recycle suspended solids concentration, wt %	2.0	2.0
Effluent Soluble BOD_5,[b] mg/l	900	45

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[a] Preliminary information supplied by Union Carbide on the basis of assumptions provided by WPA.

[b] Used as basis for determining oxygen requirement.

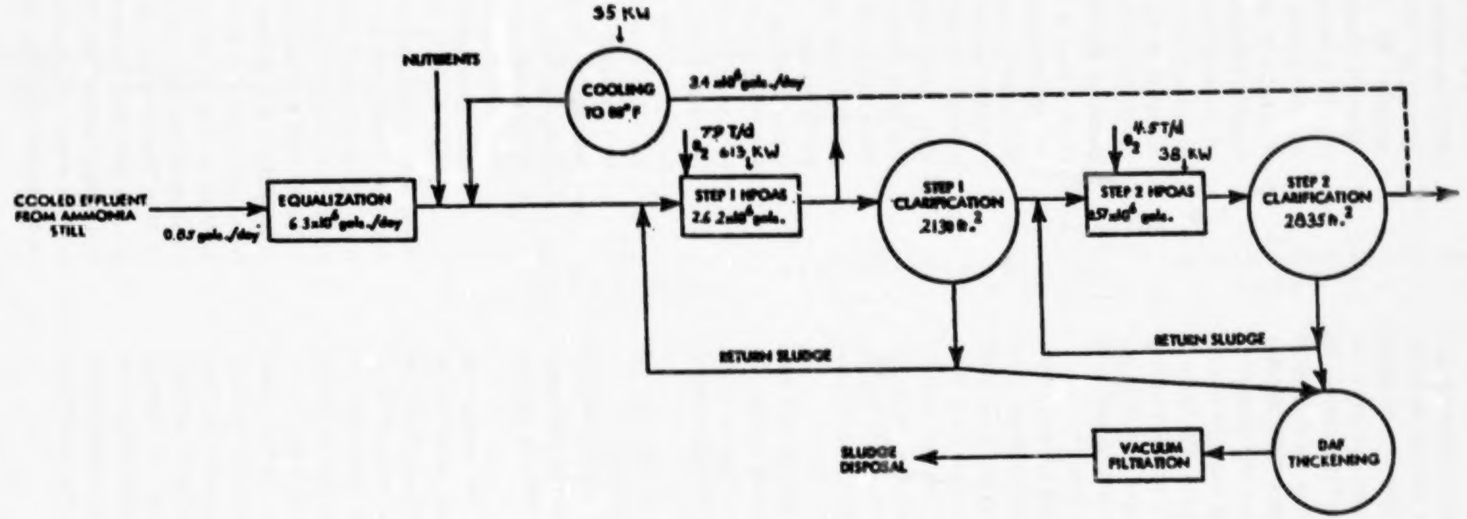
COOLED EFFLUENT FROM AMMONIA STILL
0.85 gals./day
EQUALIZATION
6.3x10^6 gals./day
NUTRIENTS
35 KW
COOLING TO 80°F
3.4 x10^6 gals./day
79 T/d
O2 613 KW
STEP 1 HPOAS
2.6 2x10^6 gals.
STEP 1 CLARIFICATION
2130 ft.²
4.5 T/d
O2
38 KW
STEP 2 HPOAS
.57x10^6 gals.
STEP 2 CLARIFICATION
2835 ft.²
RETURN SLUDGE
RETURN SLUDGE
DAF THICKENING
VACUUM FILTRATION
SLUDGE DISPOSAL

Figure 6. High purity oxygen activated sludge (HPOAS) system for Hygas plant with lignite feed.

cooling by forced evaporation. The unanswered question is whether spraying will also break up and damage the biological flocs. This requires testing. Even if spraying to make droplets proves not satisfactory, it may be possible to distribute the return flow over a fill placed in the tower. This fill may be a type of cooling tower fill called "film type" (as distinct from "splash type") over which the descending water flows in a film. Most manufacturers of cooling towers make film type fill. Such a filled tower will inevitably turn into a trickling filter. Munters Corporation makes a plastic fill that has been used, in separate situations, in a cooling tower and in a trickling filter.

In Figure 7 is shown a possible scheme with a combined cooling tower/trickling filter. The new unit will be designated as an activated trickling filter (ATF). An activated trickling filter as used here is a trickling filter of plastic medium loaded continuously with the mixed liquor from the HPOAS units, as shown in Figure 7. The ATF is expected to achieve the following objectives:

1. Reduce BOD by about 30 percent as a pretreatment to the HPOAS system;
2. Reduce the temperature of the recycled mixed liquor from the HPOAS system from about 95° to 80° F;
3. Strip off the excessive carbon dioxide from the recycled mixed liquor.

Qualitatively, the use of an ATF-HPOAS system may be expected to have the following advantages over the use of an HPOAS system alone:

1. Less energy required. The energy required to pump water and drive the air fans in the ATF may be lower than that to transfer the large quantities of air or to generate and transfer adequate oxygen for the activated sludge process;
2. Less capital and operating costs;
3. Less system upsets and higher treatment reliability. This is due to the fact that fixed biological growth is less susceptible to loss of the biota activity through shock loadings of either hydraulic feed, BOD concentration, or toxicants. Recycling of the mixed liquor may also contribute to the treatment reliablity.

In the design of ATF we used the BOD removal relationship for trickling filters of plastic medium, and the details of calculation have been reported elsewhere.[5] However, the use of ATF in combination with an HPOAS system in the manner shown in Figure 7 results in an extremely high organic loading of about 8,000 lb BOD/(10^3ft^3 of medium)(day) compared to current practice of having high organic loadings in the range of 1,000-1,400 lb BOD/(10^3ft^3)(day). This occurs because the BOD concentration in the feed water is high and, also, because the recirculation rate is determined by the cooling requirement of step 1 of the HPOAS sysem and is not adjusted to control the BOD loading of the trickling filer. Also, there are contaminants in the coal conversion wastewater other than phenol which may inhibit biochemical oxidation in the ATF to some extent. For these reasons, the usual trickling filter design equation has been modified by assuming that the reduction in BOD obtained is only 30 percent instead of the 80 percent found by use of the standard design equation. Furthermore, forced ventilation is used to avoid oxygen transfer limitation. In our preliminary design modular units of ATF designed for ease of counter-flow ventilation, each 20 feet in diameter and 18 feet in height, have been used.

According to B.F. Goodrich General Products, who manufactures plastic medium for trickling filters, no difficulty is anticipated in running the mixed liquor through the filter medium as long as the MLSS does not exceed 10,000 mg/l and the diameter of solid particles is less than 0.5 inches. Nevertheless the detailed configuration of ATF remains to be better defined in the future pilot tests. The critical considerations may be how to prevent plugging of the filter medium by excessive biological growth and how to avoid the anaerobic condition when oxygen transfer becomes limiting. In spite of these uncertainties we strongly recommend experimenting with ATF as successful

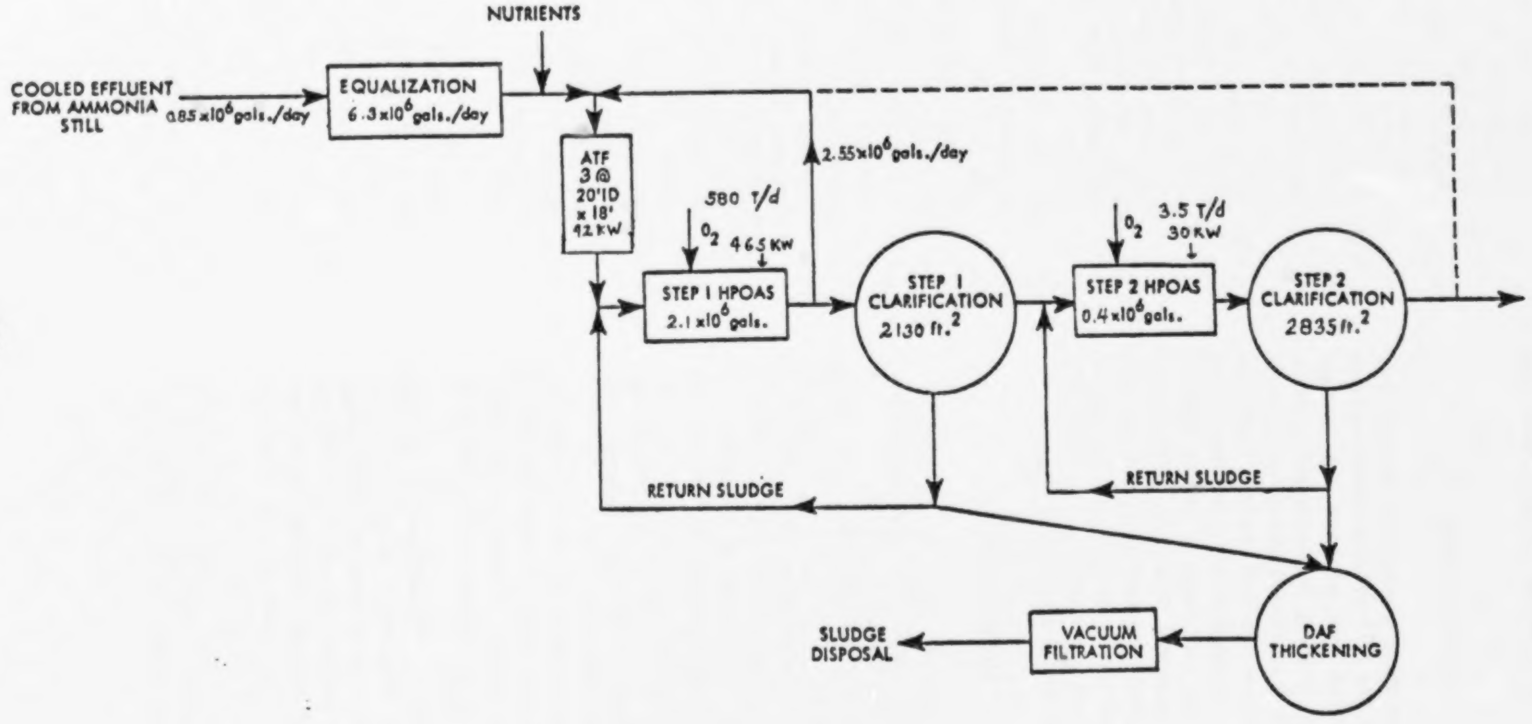
COOLED EFFLUENT FROM AMMONIA STILL
0.85 x10^6 gals./day
EQUALIZATION
6.3x10^6 gals./day
NUTRIENTS
ATF
3 @
20'ID
x 18'
42 KW
580 T/d
0_2
465 KW
STEP 1 HPOAS
2.1 x10^6 gals.
2.55x10^6 gals./day
STEP 1
CLARIFICATION
2130 ft.^2
0_2
3.5 T/d
30 KW
STEP 2 HPOAS
0.4x10^6 gals.
STEP 2
CLARIFICATION
2835 ft.^2
RETURN SLUDGE
RETURN SLUDGE
DAF
THICKENING
VACUUM
FILTRATION
SLUDGE
DISPOSAL

Figure 7. Activated trickling filter-high purity oxygen activated sludge system (ATF-HPOAS) for Hygas plant with lignite feed.

applications of a similar system have been reported.[15]

CONCLUSIONS

Among the three preliminary designs described above, the ATF-HPOAS system appears to be the most cost-effective and energy-effective[5] for treating high-strength wastes such as those from Hygas plants using lignite feed. With bituminous coal feed the BOD concentration will be much smaller, and the cooling of mixed liquor from step 1 of the HPOAS becomes unnecessary. The use of HPOAS may be preferred to AAS where oxygen is also utilized in the coal conversion process. The use of mutated bacteria and experimenting with ATF are recommended for future pilot tests.

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SOLUBILITY AND TOXICITY OF POTENTIAL POLLUTANTS IN SOLID COAL WASTES

By
R. A. Griffin[1], R. M. Schuller[1], J. J. Suloway[2],
S. A. Russell[1], W. F. Childers[2],
and N. F. Shimp[1]

[1]Illinois State Geological Survey
[2]Illinois Natural History Survey
Urbana, Illinois

Abstract

Chemical and mineralogical characteristics of a LURGI gasification ash and an H-Coal liquefaction residue from the Illinois Herrin (No. 6) Coal Member are related to chemical solubility at several pH's and to biological toxicity of aqueous supernatant solutions. Chemical analyses were performed for some 60 constituents. The major constituents in the solid residues were Al, Ca, Fe, K, and Si. Large quantities of Mg, Mn, Na, S, and Ti and significant quantities (10-1000 ppm) of trace metals were also present.

The minerals detected in the liquefaction solid wastes included quartz, pyrrhotite, sphalerite, calcite, anhydrite, wollastonite, and clay minerals. A small amount of quartz and calcite reacted to form wollastonite, and nearly all the pyrite present in the feed coal was converted to pyrrhotite during conversion. The minerals detected in the LURGI ash included quartz, mullite, plagioclase feldspar, and hematite. Nearly all the pyrite present in the feed coal was converted to hematite during gasification. Clays were converted to mullite, and other accessory minerals were apparently converted to feldspars.

Of the approximately 60 chemical constituents measured in the raw LURGI ash, only 15 were found to be soluble enough to excede recommended water quality levels, even at pH values as low as 3. Six of these constituents—Al, Cr, Co, Cu, Fe, and Zn—exceeded the recommended values for natural waters only when the pH was quite acid. Over the pH range 3-10, the remaining nine—B, Ca, Cd, K, Mn, NH_4, Pb, SO_4, and Sb—exceeded the recommended levels in all solutions. These 9 are thought to pose the highest potential pollution hazard.

The results of 96-hour static bioassays indicated that the water-soluble constituents in equilibrium with the wastes were not acutely toxic to young fathead minnows at near-neutral pH's (7.0-8.5); however, in both the high- and low-pH solutions all the minnows died. Mortality may have been the combined result of pH and total ion content. Further studies of the causes of the fathead minnow mortality are being conducted.

INTRODUCTION

The potential need for development of a coal gasification and liquefaction industry in the United States has been dramatically demonstrated by the widespread shortages of natural gas and fuel oil during the winter of 1977. Because the production of clean fuel from coal is not without environmental impacts, assessment of potential impacts of coal conversion plants is underway (e.g., Sather et al., 1975; Forney et al., 1975; and Jahnig and Bertrand, 1976). Such studies have emphasized the effects of coal conversion upon air pollution. Although these problems are serious, they have tended to overshadow another important matter—the potential pollution of water resources.

Solid Coal Wastes As Sources of Pollutants

One by-product of coal conversion is the generation of solid wastes For example, a commercial coal gasification plant with a capacity of 250 million cubic feet of gas per day will use about 8 million tons of coal and will generate about 2.3 million tons of ash and dry refuse per year (Sather et al., 1975). The amount of residue generated by a single coal gasification plant has been estimated to occupy an area of 625 acre feet per year and in 20 years would cover 1250 acres to a depth of 10 feet (Seay et al., 1972, and Asburg and Hoglund, 1974). The disposal of these huge amounts of solid waste is unprecedented, and successful commercial production of synthetic gas by these processes will depend, in part, on the environmental acceptability of disposal of the solid-waste residues.

Interest in the potential pollution hazard from the accessory elements contained in the solid wastes is increasing. About 60 of these elements are found in concentrations of less than 1 ppm to several percent (Gluskoter et al., 1977). These accessory elements in the coal are either retained in the gasifier ash or are removed by downstream scrubbing of the raw gases. The ultimate disposal of the ash and downstream processing wastes will probably be in tailings ponds and landfills. The types and quantities of solid wastes from several proposed gasification processes are given in Table 1.

Consideration must be given to undesirable accessory elements that might be leached from the wastes during handling in water slurries. Even those wastes handled dry will ultimately be exposed to leaching by ground water when landfilled. Potentially severe contamination from accessory elements contained in the ash may also result from the disposal of refuse from the cleaning of coal prior to gasification or liquefaction. It is well-known that iron sulfates and acids are produced from the oxidation of pyritic minerals contained in the refuse when exposed to air (e.g., Singer and Stumm, 1969; Smith et al., 1969; and Jones and Ruggeri, 1969). Garrels and Thompson (1960) concluded that the rate of oxidation was chiefly a function of oxidation-reduction potential (Eh) and was independent of total Fe content. Similarly, Bell and Escher (1969) found that production of acidic iron salt from pyrite was an almost immediate response to the atmospheric gas composition in contact with the water. Reversing the gases from air to nitrogen caused the acid formation to decrease, and reversal from nitrogen to air caused the acid formation to increase. There is also some evidence that oxygenation of Fe (II) can be affected by the catalytic responses of trace constituents such as copper (Stauffer and Lovell, 1969).

These results have far-reaching implications for those proposals that recommend the use of alkaline gasification ashes to neutralize acid mine refuse or disposal of the ash and refuse together as landfill in strip mines. It is likely that accessory elements in the ash and refuse will be extracted by the acid solution and that these trace elements may actually catalyze the further formation of acid.

The chemical form of the accessory elements in gasification ashes and slags is important but has not been investigated thoroughly. Data on fly ashes and slags produced in coal-fired furnaces may not be pertinent because the gasification ashes and liquefaction residues are produced under different conditions, namely, at high temperatures and pressures and usually in a reducing atmosphere rather than in an oxidizing one. Significant alterations in mineralogy and chemical form of the feed coal may affect the solubility of accessory elements in the ash and thus affect their potential as pollutants.

TABLE 1

SOLID WASTES PRODUCED BY SEVERAL COAL GASIFICATION PROCESSES

Process	Type of Solid Waste	Quantity of Solid[a] (lb/hr)
BI-GAS	Water quenched Slag	68,400
CO_2 Acceptor	Water cool, Char/Spent Acceptor	496,800
HYGAS	Water cool, lock hoppers Ash/Char	138,900
Koppers-Totzek	Water quenched Slag	111,500
LURGI	Water cool, ash locks Ash	314,000
SYNTHANE	Dry let-down, fluid bed Char	362,200
U-GAS	Water cool, venturi throat Char	86,400
Winkler	Water-cooled screw conveyor Char	372,500

SOURCE: Magee, 1976.

[a] If individual values are used, Magee (1976) should be consulted to determine the original basis of computation.

Solid Coal Wastes As Resources

Another problem facing the United States is a minerals deficit that will exceed the energy deficit by the year 2000. The U.S. Department of the Interior estimates the trade deficit in minerals to be $100 billion within 25 years. The United States is almost completely dependent on foreign sources for 22 of the 74 nonenergy minerals considered essential for a modern industrial society. Of the 12 considered crucial, 7 are imported in large quantities (> 50 percent of use) (Malhotra, 1976).

Previous studies (Ruch, Gluskoter, and Shimp, 1974, and Gluskoter et al., 1975) have shown that certain minor and trace elements are concentrated in coal ash. For example, zinc occurred in certain coal ashes in concentrations as high as those mined as commercial sources. Thus, the high quantities of solid waste generated from coal gasification and liquefaction processes may be used as ore in the future. It is conceivable that the acid mine waters may be used to extract recoverable amounts of copper, nickel, zinc, iron, and other minerals from the solid wastes. Although some studies have been made in this general area (EPA, 1971), much more work is necessary to predict both the positive and negative potential environmental effects of coal conversion processes.

CURRENT STUDIES OF ACCESSORY ELEMENTS IN COAL GASIFICATION AND LIQUEFACTION RESIDUES

Obtaining data concerning the accessory element content, mineralogy, solubility, and toxicity of leachates from coal solid wastes is a necessary first step in assessing the environmental aspects of coal utilization; it has not always been among the first steps taken, however (DiGioia et al., 1974). The project reported here grew out of an ongoing research effort at the Illinois State Geological Survey involving the characterization of coal and coal residues.

Data on the chemical analyses and summaries of the geological significance of over 170 coals have been published by the Illinois State Geological Survey (Ruch, Gluskoter, and Kennedy, 1971; Ruch, Gluskoter, and Shimp, 1973; Ruch, Gluskoter, and Shimp, 1974; Gluskoter et al., 1977). Current investigations are expanding these studies to include the feed coals and residues from coal conversion processes. Complete chemical, physical, and mineralogical characterizations of slags, ashes, chars, cleaning wastes, and residues from various coal gasification and liquefaction processes are being made. These chemical and mineralogical characteristics are then being related to chemical solubilities at several pH's and to biological toxicity of aqueous extracts of the solid-waste residues. This report presents some recent data obtained from a LURGI gasification ash and an H-Coal liquefaction residue from an Illinois No. 6 Coal.

Sources of Gasification Ash and Liquefaction Residue

During 1973 and 1974, the American Gas Association and the Office of Coal Research studied the performance and suitability of various American coals for gasification by the LURGI process. Four different coals were sent to Scotland, where they were gasified in the LURGI plant at Westfield. Among the four coals were 5000 tons of Herrin (No. 6) coal from Illinois that was gasified; the unquenched waste ash was then sent back to the United States for analyses. The sample of LURGI ash from the No. 6 Coal, for which data is reported here, was supplied by Peabody Coal Company's Central Laboratory at Freeburg, Illinois.

The coal liquefaction residue was obtained from Hydrocarbon Research, Inc., Trenton, New Jersey. The residue comprised the vacuum still bottoms generated during production of a fuel oil product using an Illinois No. 6 Coal and the H-Coal^R PDU at the HRI Trenton Lab on May 3, 1976.

Chemical and Mineralogical Characterization

The chemical composition of the H-Coal residue and the LURGI ash has been determined for approximately 60 constituents and is summarized in Tables 2 and 3. The major constituents found were Al, Ca, Fe, K, and Si. Large quantities of Mg, Mn, Na, S, and Ti and significant quantities (10-1000 ppm) of trace metals were also present.

The minerals detected in the LURGI ashes by X-ray diffraction included quartz, mullite, hematite, and plagioclase feldspar. Nearly all

TABLE 2

CHEMICAL COMPOSITION OF LURGI ASH AND SLURRY SUPERNATANT SOLUTIONS OF THE ASH FROM AN ILLINOIS NO. 6 COAL AT SEVERAL pH'S

Constituents	Chemical Composition of 10% Slurry Supernatant (mg/l)								Recommended Water Quality Levels (mg/l)	Solid Ash Content (mg/kg)
	Air				Argon					
pH	7.55[a]	5.10	3.82	2.68	8.82[a]	7.20	5.35	3.79	6.0 - 9.0	-
Ag	-	-	-	-	-	-	-	-	.05	< .4
Al	ND[b]	2	14	132	ND	ND	ND	92	.1	108,121
Au	-	-	-	-	-	-	-	-	-	<.001
As	ND	ND	ND	ND	ND	ND	ND	ND	.1	3
B	4.0	4.5	4.5	5.5	4.5	3.0	4.5	8.0	.75	355
Ba	ND	ND	ND	ND	ND	ND	ND	ND	1.0	950
Be	ND	ND	.01	.03	ND	ND	ND	.01	.1	12
Br	-	-	-	-	-	-	-	-	-	<1.0
Ca	290	480	400	570	440	370	430	500	50	16,652
Cd	.02	.03	.03	.06	.01	ND	.02	.05	.01	<1.6
Ce	-	-	-	-	-	-	-	-	-	140
Cl	ND	ND	ND	ND	ND	ND	ND	ND	250	100
COD[c]	2	2	2	81	2	2	16	140	50	-
MCX[d]	28	28	0	23	10	3	6	4	-	-
Cr	ND	.02	.05	.12	.01	.01	.06	.16	.05	212
Co	ND	.05	.08	.19	ND	ND	ND	.17	.05	34
Cu	.01	.02	.13	.73	.01	.05	.01	.05	.2	57
Cs	-	-	-	-	-	-	-	-	-	11
Eu	-	-	-	-	-	-	-	-	-	1.9
F	.31	.30	.09	.04	.51	.34	.16	.02	1.0	<10
Fe_{Total}	.06	.19	.24	560	.06	.11	101	880	.3	143,780
Fe^{+2}	.03	.11	.10	533	.13	.05	110	865	-	-
Ga	-	-	-	-	-	-	-	-	-	26
Ge	-	-	-	-	-	-	-	-	-	7.0
Hf	-	-	-	-	-	-	-	-	-	6.1
Hg	ND	ND	ND	ND	ND	ND	ND	ND	.0002	.05
K	42	49	51	26	39	43	48	61	5	14,611
La	-	-	-	-	-	-	-	-	-	47
Li	1.8	1.9	2.0	2.0	1.6	1.8	1.9	2.1	2.5	42
Lu	-	-	-	-	-	-	-	-	-	1.5
Mg	10.5	14	15	22	9.5	11	13.5	23	50	3,739
Mn	.45	1.94	2.7	3.8	.11	.90	2.3	3.7	.05	1,859
Mo	ND	ND	ND	ND	ND	ND	ND	ND	.01	30
Na	34	37	38	40	32	37	37	40	20[a]	1,929
NH_4	17	8	12	11	10	10	10	17	.02	-
Ni	.03	.13	.23	.50	ND	.04	.14	.42	1.	89
Pb	.1	.1	.1	.2	ND	ND	.1	.2	.03	45
P	-	-	-	-	-	-	-	-	-	87
PO_4	ND	ND	ND	ND	ND	ND	ND	ND	.05	-
Rb	-	-	-	-	-	-	-	-	-	162
S_{Total}	-	-	-	-	-	-	-	-	-	6,100
S^{-2}	ND	ND	ND	ND	ND	ND	ND	ND	.002	1,500
SO_4	820	943	808	338	730	735	700	710	250	8,100
Sb	.2	.3	.3	.6	.3	.3	.3	.5	.05	4.2

TABLE 2 (Continued)

Sc	-	-	-	-	-	-	-	-	-	29
Se	-	-	-	-	-	-	-	-	.01	< 1
Si	5	29	60	130	4	9	27	120	-	229,946
Sm	-	-	-	-	-	-	-	-	-	10
Sn	ND	ND	ND	ND	ND	ND	ND	ND	-	-
Sr	1.8	1.9	2.1	2.9	1.5	1.7	1.9	2.6	50.	370
Ta	-	-	-	-	-	-	-	-	-	1.1
Te	ND	ND	ND	ND	ND	ND	ND	ND	-	-
Th	-	-	-	-	-	-	-	-	-	21
Ti	ND	ND	ND	ND	ND	ND	ND	ND	-	6,295
Tl	ND	ND	ND	ND	ND	ND	ND	ND	-	4.6
U	=	=	=	-	=	=	=	-	-	17
V	-	-	-	-	-	-	-	-	0.1	184
W	-	-	-	-	-	-	-	-	-	1.5
Yb	-	-	-	-	-	-	-	-	-	2.9
Zn	.12	5.5	12	17	.01	.11	6.5	20	.2	400
Zr	-	-	-	-	-	-	-	-	-	170
EC (mmhos/cm)	1.17	1.50	1.95	5.60	1.20	1.39	1.80	5.20	18	-
Eh (electrode mv)	+223	+246	+407	+349	+109	+161	+102	+243	-	-

[a] Natural pH of supernatant [b] Not detectable [c] Chemical oxygen demand [d] Methylene chloride extractable [e] For low Na diet; 250 ppm for taste

TABLE 3

CHEMICAL COMPOSITION OF H-COAL LIQUEFACTION WASTE AND SLURRY SUPERNATANT SOLUTIONS OF THE WASTE AT SEVERAL pH'S

Constituents	Solid Ash Content (mg/kg)	Chemical Composition of 10% Slurry Supernatant (mg/l)								Recommended Water Quality Levels (mg/l)
		Air				Argon				
pH	—	8.83[a]	8.16	5.01	3.14	11.31[a]	8.50	5.53	2.30	6.0 - 9.0
Ag	0.16	—	—	—	—	—	—	—	—	.05
Al	17,253	3.0	<.5	<.5	5.5	1.5	<.5	1.5	5.7	.1
Au	—	—	—	—	—	—	—	—	—	—
As	1.5	<1	<1	<1	<1	<1	<1	<1	<1	.1
B	300	11.0	13.0	11.6	13.6	11.0	12.2	12.9	15.0	.75
Ba	40	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.0
Be	1.8	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	.1
Br	6.7	—	—	—	—	—	—	—	—	—
Ca	7862	110	175	380	497	133	155	425	487	50
Cd	<.4	<.03	<.03	<.03	<.03	<.03	<.03	<.03	<.03	.01
Ce	16	—	—	—	—	—	—	—	—	—
Cl	1000	75	71	67	75	78	70	75	64	250
COD[b]	—	15	9	7	15	24	8	2	24	50
Cr	27.5	<.02	<.02	<.02	.03	<.02	<.02	<.02	.05	.05

TABLE 3 (Continued)

Co	4.45	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	.05
Cu	14	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05	.2
Cs	1.7	—	—	—	—	—	—	—	—	—
Eu	0.69	—	—	—	—	—	—	—	—	—
F	100	1.00	1.15	0.60	0.86	0.70	1.20	0.85	0.84	1.0
Fe_{Total}	73,662	<.1	<.1	14	31.5	<.1	<.1	6.5	90	.3
Fe^{+2}	—	<.1	<.1	11	29.5	<.1	<.1	.9	90	—
Ga	4.6	—	—	—	—	—	—	—	—	—
Ge	4.9	—	—	—	—	—	—	—	—	—
Hf	0.86	—	—	—	—	—	—	—	—	—
Hg	—	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	.0002
K	2490	1.4	1.4	2.1	2.8	1.2	1.5	2.0	2.5	5
La	9.8	—	—	—	—	—	—	—	—	—
Li	—	<.01	.01	.02	.02	<.01	.01	.02	.02	2.5
Lu	.024	—	—	—	—	—	—	—	—	—
Mg	844	0.5	0.6	2.7	4.0	0.6	0.8	3.0	4.0	50
Mn	77	<.02	.04	1.67	2.68	<.02	0.10	1.83	2.52	.05
Mo	6.4	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2	.01
Na	619	6.7	7.0	7.5	9.3	6.5	6.8	109[c]	9.0	20[d]
NH_4	—	9	6	8	8	8	5	7	5	.02
Ni	21	<.07	<.07	<.07	<.07	<.07	<.07	<.07	.25	1.0
Pb	32	<0.1	<.1	.2	.25	<.1	<.1	.15	.2	.03
P	44	—	—	—	—	—	—	—	—	—
PO_4	—	<.025	<.025	<.025	<.025	<.025	<.025	<.025	0.1	.05
Rb	16	—	—	—	—	—	—	—	—	—
S_{Total}	18,000	—	—	—	—	—	—	—	—	—
S^{-2}	300	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2	.002
SO_4	600	65.5	68.5	148.5	96.5	65.5	66.0	70.5	73.5	250
Sb	1.2	<.4	<.4	<.4	<.4	<.4	<.4	<.4	<.4	.05
Sc	4.1	—	—	—	—	—	—	—	—	—
Se	—	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	.01
Si	39,641	<1	<1	<1	3	<1	<1	<1	3	—
Sm	2.3	—	—	—	—	—	—	—	—	—
Sn	0.6	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	—
Sr	30	.20	.24	.34	.50	.20	.26	.38	.48	50
Ta	0.17	—	—	—	—	—	—	—	—	—
Te	<0.1	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	—
Th	3.5	—	—	—	—	—	—	—	—	—
Ti	1019	<.6	<.6	<.6	<.6	<.6	<.6	<.6	<.6	—
Tl	1.7	<.4	<.4	<.4	<.4	<.4	<.4	<.4	<.4	—
U	5.7	—	—	—	—	—	—	—	—	—
V	33	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	0.1
W	4.4	—	—	—	—	—	—	—	—	—
Yb	1.0	—	—	—	—	—	—	—	—	—
Zn	71	.01	.01	.06	.27	.02	.02	.12	.76	.2
Zr	41	—	—	—	—	—	—	—	—	—
EC (mmhos/cm)	—	0.05	0.87	2.18	2.83	0.68	1.00	2.51	3.49	18
Eh (electrode mv)	—	+202.8	+235	+295.1	+419.6	+13.9	+178.9	+233.7	—	—

[a] Natural pH of supernatant [b] Chemical oxygen demand [c] NaOH added for pH adjustment [d] For low Na diet; 250 ppm for taste

the pyrite present in the feed coal was converted to hematite during gasification. The clay minerals present in the feed coals were not detected in the ash and were apparently converted to mullite, a high-temperature-phase aluminosilicate. The other accessory minerals were apparently converted to a feldspar.

The minerals detected in the H-Coal residue samples by X-ray diffraction included quartz, pyrrhotite, sphalerite, calcite, anhydrite, illite, kaolinite, and some expandable clay minerals. Wallastonite ($CaSiO_3$), undetected by X-ray diffraction, was found by the scanning electron microscope with the energy-dispersive X-ray analyzer in polished and etched samples of heavy minerals from the H-Coal residues.

Several minerals participate in chemical reactions during coal conversion processes. For example, in the H-Coal process, a small amount of quartz and calcite reacted to form wollastonite. More importantly, nearly all the pyrite present in the feed coal was converted to pyrrhotite in the solid waste. This occurred at temperatures lower than would be expected from comparisons with published data on reactions of pure iron sulfides at equilibrium conditions. These reactions could have occurred in the slurry preheaters or in the liquefaction process reactors. The pyrite-to-pyrrhotite conversion might have been a result of the cobalt-molybdate catalyst, which is used for conversion of organic constituents to a fuel oil product in the H-Coal process, but the effect of the catalyst on the mineral interactions is not known. We have also studied other liquefaction process residues and the change from pyrite to pyrrhotite also occurred without the aid of the catalyst in the Solvent Refined Coal (SRC) process. The SRC process does not use a catalyst. In the three liquefaction processes studied (H-Coal, SRC, and SYNTHOIL), nearly all pyrite in the feed coals was converted to pyrrhotite in the solid residues. This conversion may be the result of intimate association of the hydrogen in the liquefaction system with the pyrite in the coal slurry. Established phase relationships in closed systems cannot be directly applied to mineral matter in the liquefaction processes because of the undefined interactions of the components and the removal of vapor from the system during reactions. Therefore, mineral reactions must be deduced from a thorough study of the coal mineral matter before and after coal conversion.

Aqueous Solubility

Probably the single most important factor affecting the solubility of the accessory elements in coal solid wastes is pH. Many coal wastes contain sulfide minerals that can acidify upon exposure to air. In terms of heavy metals, solid wastes disposed of in acidic strip or underground mines are potentially more soluble than wastes disposed of under neutral or alkaline conditions.

The oxidation potential (Eh) is also an important factor affecting the solubility of minerals (Garrels and Christ, 1965). When solid wastes are buried underground or in water-saturated materials, anaerobic (oxygen deficient) conditions usually develop. Studies of the effect of Eh and pH on the solubilities of coal solid wastes could produce data that would allow prediction of potential pollution hazards or, on the other hand, prediction of optimum conditions for extraction of the potentially valuable elements contained in the wastes.

The current experimental design involved making 10% aqueous slurries of each of the solid wastes studied. The slurries were set up in series that had been adjusted to four individual pH values over the range 2 to 11. The pH values of the slurries were monitored daily and readjusted to the specified value if necessary. Chemical equilibrium was assumed when the pH values remained constant. This process took approximately 3 months; however, studies with LURGI ashes from three different coals showed that chemical equilibrium was more than 90 percent complete in one week.

Duplicate sets of slurries were used. One set was equilibrated under an argon (oxygen and CO_2 free) atmosphere and the second set was equilibrated under an air (oxidizing) atmosphere. The results for a LURGI ash and an H-Coal residue obtained from an Illinois No. 6 Coal are reported in Tables 2 and 3. Tables 2 and 3 contain the measurements for some 63 chemical constituents measured in the solid ash and in the aqueous supernatant solutions. Also included in the tables is a summary of recommended water quality levels (EPA, 1973) for as many constituents for which data could be found. This was done for comparison with the water solubility levels found under conditions given in Tables 2 and 3.

Potential Pollutants

Of the approximately 60 chemical constituents measured in the raw LURGI ash and H-Coal residue (Tables 2 and 3), about 31 were found to be present at concentrations that could present a potential hazard. The remainder were present at such low levels that, even if completely soluble, they would pose no particular problem. Of the 31 that were a potential problem, 16 were found to be in forms soluble enough to exceed recommended water quality levels in some samples at pH values between 3 and 8. These 16 constituents are listed in Table 4. Seven of the constituents—Al, Cr, Co, Cu, F, Fe, and Zn—exceeded the recommended levels in water only under certain pH conditions, generally when the pH was quite acid. The other nine constituents—B, Ca, Cd, K, Mn, NH_4, Pb, SO_4, and Sb—exceeded the recommended levels in all LURGI ash solutions over the pH range 3 to 9. These nine constituents are thought to represent the highest potential pollution hazard. Discharges of the 16 constituents listed in Table 4 at the levels found in this study could cause some environmental degradation and require some form of wastewater treatment.

Toxicity Studies

The acute toxicities of the water-soluble con-

TABLE 4

ELEMENTS EXCEEDING RECOMMENDED WATER QUALITY LEVELS

	LURGI Ash Solubility		H-Coal Residue Solubility		
Constituent	pH 3 (mg/l)	pH 8 (mg/l)	pH 3 (mg/l)	pH 8 (mg/l)	Recommended Levels (mg/l)
Al	132.	<0.5	5.5	<0.5	0.10
B^a	5.5	4.0	13.6	13.0	0.75
Ca^a	570.	290.	497.	175.	50.
Cd^a	0.06	0.02	—	—	.01
Cr	0.12	<0.02	—	—	0.05
Co	0.19	<0.10	—	—	0.05
Cu	0.75	0.01	—	—	0.20
F	—	—	0.86	1.15	1.00
Fe	560.	0.06	31.50	<0.10	0.30
K^a	26.	42.	—	—	5.00
Mn^a	3.80	0.45	2.68	0.04	0.05
NH_4^a	11.	17.	8.	6.	0.02
Pb^a	0.20	0.10	0.25	<0.10	0.03
SO_4^a	338.	820.	—	—	250.
Sb^a	0.60	0.20	—	—	0.05
Zn	17.00	0.12	0.27	0.01	0.20

^{a}Highest pollution potential

stituents in the solid-waste leachates from coal conversion were assayed, used fathead minnows, *Pimephales promelas*. Three-to-six-day-old free-swimming fatheads were used for the 96-hour static bioassays. These studies were performed under controlled conditions in an environmental chamber, using procedures suggested by the Committee on Methods for Toxicity Tests with Aquatic Organisms (1975). All bioassays were replicated one or more times.

The toxicities of the water-soluble compounds in equilibrium with the H-Coal liquefaction residue and the LURGI gasification ash at various pH values are shown in Figure 1. The waste leachates do not appear acutely toxic to young fathead minnows at near-neutral pH's (7.0-8.5); however, 100 percent mortality occurred in both the high- and low-pH solutions (Figure 1). To test only the pH effect on the mortality of the fathead minnows, bioassays were conducted using buffered solutions of reconstituted water ranging in pH from 5.0 to 11.0. The results of these bioassays (Figure 1) were similar to those found for the waste leachates. It is possible that most of the mortality observed was the result of pH values. However, the higher mortality observed in the alkaline range for the H-Coal leachate than for the reconstituted water indicates a toxicity that is not accounted for by pH values.

Attempts were made to decrease the mortality due to pH effects by neutralizing some of the acidic leachate solutions with NaOH. In all cases 100 percent mortality occurred even though the pH was neutral. All the neutralized solutions had specific conductance values greater than 7.00 mmhos/cm. We hypothesized that the high total ion concentration resulted in ionic shock and was responsible for the mortality in the neutralized solutions. This conclusion was verified by a study in which the specific conductance of several solutions of reconstituted water was varied by the addition of NaCl. The results are shown in Figure 2.

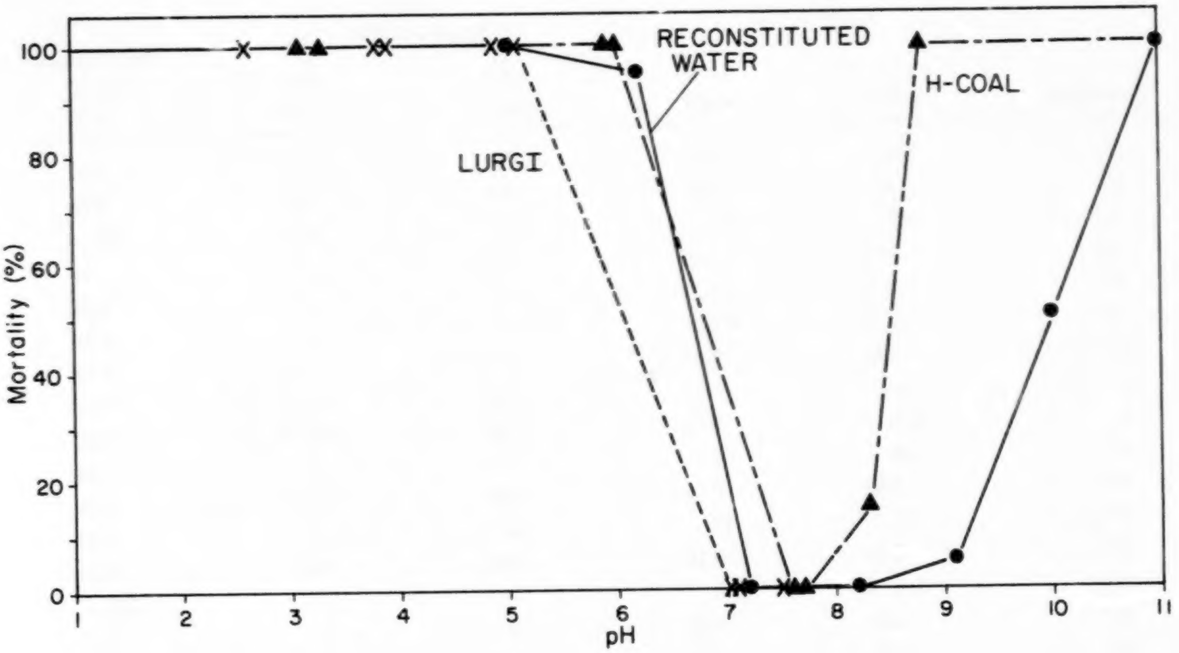

Figure 1. Effect of pH on the mortality of fathead minnows in LURGI ash leachate, H-Coal residue leachate, and reconstituted water.

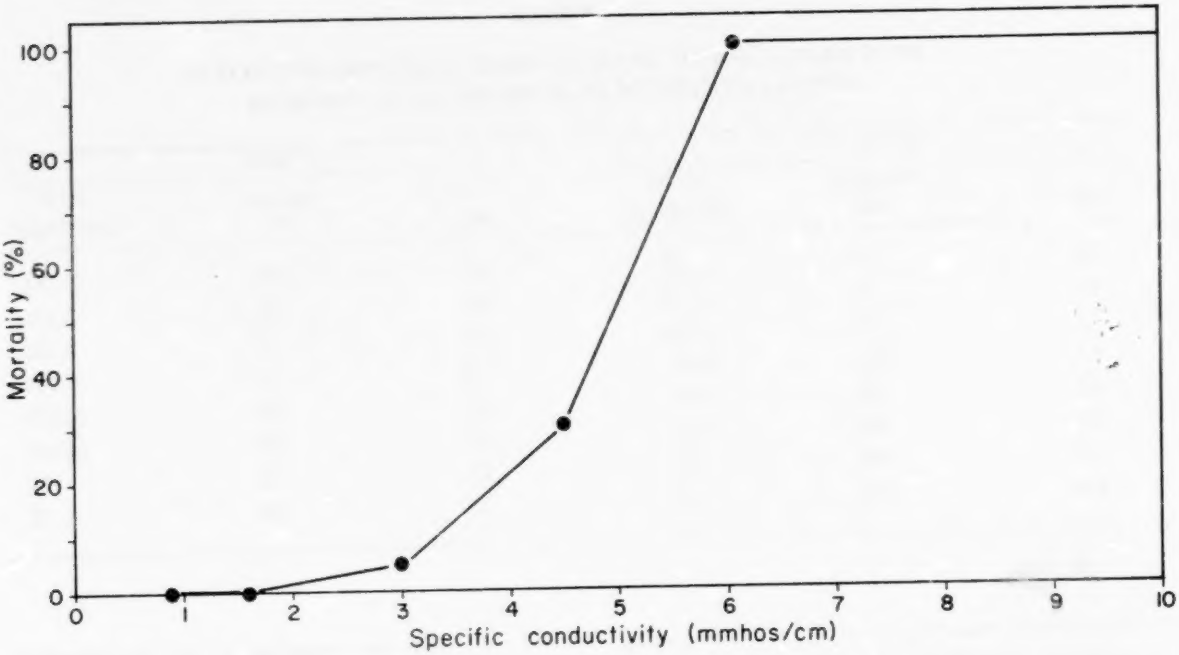

Figure 2. **Effect of specific conductance on the mortality of fathead minnows in reconstituted water.**

Solutions with a specific conductance greater than 6.10 mmhos/cm caused 100 percent mortality.

The LC-50's were determined for the waste leachates and are presented in Table 5. The LC-50 is the number of milliliters of waste material per 100 milliliters of total volume that results in the death of 50 percent of the test organisms during 96 hours. For example, if the LC-50 is 5.0 ml/100ml, then a solution of 5.0 ml of waste leachate and 95.0 ml of reconstituted water will kill 50 percent of the fathead minnows. If the LC-50 is greater than 100ml/100ml, a solution of undiluted leachate will not kill 50 percent of the minnows. The approximate LC-50 values for the H-Coal and LURGI ash leachates of various pH's are listed in Table 5. Very acidic solutions (pH <4.0) must be diluted 20 or more times to decrease mortality to 50 percent, whereas full-strength near-neutral solutions were not toxic.

These studies indicate that the water-soluble constituents in equilibrium with wastes at near-neutral pH's (7.0-8.5) are not acutely toxic to young fathead minnows. Both pH and total salt concentration do appear to be important factors that affect the observed mortality of the young minnows. Further studies are being conducted to determine the interactions of pH, total ion concentration, and toxic compounds extracted from the wastes.

RECOMMENDATIONS

The potential environmental and economic consequences associated with the disposal of the solid wastes generated by even a single large-scale coal conversion facility is impressive because of the sheer magnitude of the wastes generated. The major solid wastes are the refuse from coal cleaning; ashes, slags, and chars from the conversion process; and sludges from water cleanup. Clearly, careful planning is required to mitigate adverse en-

TABLE 5

PERCENTAGE MORTALITY AND APPROXIMATE LC-50'S FROM BIOASSAYS OF FATHEAD MINNOWS FOR LURGI ASH AND H-COAL LEACHATES

LURGI			H-COAL		
pH	Mortality (%)	LC-50 (ml/100 ml)	pH	Mortality (%)	LC-50 (ml/100 ml)
7.5	0	>100	8.8	100	50-100
7.1	0	> 100	8.3	15	>100
7.1	0	> 100	7.7	0	> 100
5.1	100	25-50	7.6	0	> 100
4.9	100	5-25	6.0	100	50-100
3.9	100	5-25	5.9	100	50-100
3.8	100	<5	3.3	100	<5
2.6	100	<5	3.1	100	<5

vironmental impacts; however, planning can be effective only when an adequate data base is available.

Specific research needs include the qualitative and quantitative characterization of coal conversion solid wastes:

1. Quantitative determination of the accessory elements contained in the wastes
2. Determination of the solubility of the accessory elements under a variety of environmental conditions
3. Establishment of the effects of coal characteristics and process operating variables on the character of the solid wastes generated by a given process
4. Determination of methods for recovering valuable metals from the solid wastes
5. Determination of the ultimate fate of waterborne pollutants resulting from solid-waste materials
6. Characterization and quantification of both the acute and chronic biological toxicity and public health hazard associated with pollutants from coal solid wastes
7. Pursuit of research to establish environmental standards that will maintain the integrity of the environment within realistic bounds

The energy demands of the nation are such that construction of large-scale coal gasification and liquefaction plants will be undertaken. The process designs are at the pilot plant stage of development and demonstration plants will undoubtedly be built within the next decade. There are few precedents with which to predict the environmental impact of the disposal of waste products on a scale this large. It is expected that valuable trace elements can be recovered from many wastes if proper planning is provided. Basic and applied research is needed to develop the technical information necessary to formulate those strategies and disposal options necessary to avoid serious problems that could appear suddenly in large-scale operations. Further, the research must be begun soon so that the data will be available for the planning of the initial large-scale coal conversion facilities.

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APPLICABILITY OF COKE PLANT WATER TREATMENT TECHNOLOGY TO COAL GASIFICATION

William A. Parsons, Director,
Corporate Environmental Services,
Arthur G. McKee & Company,
Cleveland, Ohio

Walter Nolde, Technical Manager,
By-Product Plants, McKee-Otto Engineers
and Constructors, Cleveland, Ohio

Abstract

Historically, some of the most profound early waste treatment research was performed in Europe on liquors from coke and gas plants. The early studies demonstrated that wastewater technology developed for coal gas, producer gas, and by-product coke plants was transferable. It follows that much of wastewater treatment technology developed recently for by-product coke plants will be transferable to tar-producing coal gasification processes. It is expected that the development of virgin wastewater treatment technology will be required for coal gasification processes that operate under tar-free conditions.

Activated sludge technology is adaptable to treatment of condensates from tar-producing coal conversion processes. The application of the data base available from coke plant waste treatment will reduce a research project to a developmental project at a vast saving in time and effort. Coal condensates may be deficient in trace element nutrients such as phosphorous, magnesium, and potassium. Evaluation of nutrient adequacy is recommended in developmental studies. Effluent polishing by dissolved air flotation is worthy of consideration inasmuch as the process is more capable of handling slugs of suspended solids than are filters. In addition, the float separated from the flotation process is a concentrate rather than a dilute filter backwash.

Preliminary absorption of halides is a concept that has potential for improving water management at coal gasification facilities. The separation of a low volume, high salt concentrate would reduce disposal problems and increase the feasibility of water reuse.

Gas lighting with coal-derived gas and waterborne collection of sewage commenced in the cities and towns of England in the early nineteenth century. The technology soon spread throughout Europe and to the Americas. The adoption of gas and sewage technology in conjunction with a large increase in population resulted in gross pollution of receiving waters. A Royal Commission on Sewage Disposal was appointed in 1898 to report on methods for the treatment and disposal of sewage and trade wastes. Not surprisingly, coal gas plant liquors were among the trade wastes included in the early investigations. The evolution of the studies has been documented elsewhere[1,2,3].

A review of highlights of previous studies would show that near the turn of the century studies with biological filters had determined that spent ammonia liquor from a gas plant could be treated as a 0.5 percent admixture with domestic sewage. By 1911, it had been demonstrated experimentally that gas plant ammonia liquor could be treated for substantial periods on biological filters by recirculation of effluent without a requirement for dilution with sewage. The experiments employed recirculation ratios of up to 19 to 1 and preceded by 25 years the frenzied rush in the domestic sewage field to patent every conceivable recirculation scheme for biological filtration.

The treatment of coke plant ammonia still waste in admixture with domestic sewage was tested early in the evolution of the activated sludge process. Based on experiments at Milwaukee in 1920 and subsequent studies, Mohlman[4] concluded that admixtures containing 30 to 40 mg/l of phenol were acceptable for the activated sludge process. He also concluded that admixtures containing 25-35 mg/l phenol were acceptable for intermittent sand filtration. Nolte[5] in the early Thirties, employed the addition of nutrient phosphate to ammonia liquor to enable experimental treatment by activated sludge without domestic sewage dilution.

The recognition of the nutritional deficiency of ammonia still waste was an important observation inasmuch as the performance of biological treatment on undiluted waste had been unreliable over sustained periods of operation. Prototype activated sludge plants were installed at coke plants in Europe and

North America in the early Sixties[6,7,8,9]. The treatment performance has been highly impressive but problems have been experienced in regard to consistency. Activated sludge installations at coke plants have proliferated in recent years.

Thus an analysis of early research on biological treatment of ammonia liquor suggests that the trend of original studies tended to be on liquors from coal gas plants. The result of the studies were somewhat inconsistent but were shown to be transferable to coke plants and to producer gas plants. It follows that many of the refinements in biological treatment more recently developed at coke plants will be transferable to tar producing coal gasification technology. Tar-free coal conversion processes are expected to require the development of virgin waste treatment technology.

Improved gas cleaning technology is being installed at modern coke plants. Coke plant gas cleaning technology is expected to be applicable to the cleaning of cooled producer gas for industrial consumption, but modification would generally be required for the production of substitute natural gas from coal for interstate pipeline transmission.

CURRENT STATUS

Gas Cleaning

Upgraded gas cleaning and water treatment technology have been employed in recent coke plant installations. A generalized block diagram representative of coke plant gas cleaning is given as Figure 1. Primary cooling to about 90° F is advocated to provide for early removal of naphthalene to minimize deposition of naphthalene during gas transport. High efficiency electrostatic tar removal with back-up capability is employed to protect subsequent by-product processes. The selection of the ammonia recovery process depends upon projections of marketability of the recovered by-products, and gas quality criteria. Some recent plants employ the Phosam process for indirect recovery of ammonia as anhydrous ammonia—which offers maximum flexibility for the marketing of the by-product. However, the simpler recovery of ammonia as ammonium sulfate is still the most popular method. When coke plants recover sulfur as sulfuric acid, some of the acid can be consumed in the ammonium sulfate by-product operation.

The trend at modern coke plants for desulfurization has been to employ neutralization processes using ammonia liquor or other alkalies as absorbent, or oxidation processes such as Stretford. A myriad of desulfurization process alternatives exist commercially, but processes applicable to coal gas desulfurization are restricted to those that operate efficiently in the presence of extraneous sulfur and cyanide compounds. The selection of the desulfurization process is dependent upon the design of the gas treatment system and the desired by-product (e.g., H_2SO_4 or S). Neutralization processes are normally designed to achieve gas residuals of 0.1 to 0.3 gr/dscf hydrogen sulfide, whereas oxidation processes can be designed to achieve residuals of 0.01 gr/dscf hydrogen sulfide. Most of the demonstrated desulfurization processes are of limited effectiveness for the removal of organic sulfur compounds (e.g., COS and CS_2).

Ammonia Stripping

The ammonia contained in the flushing liquor condensate separated during primary cooling is recovered by steam stripping. If the coal feed contains appreciable chlorides, a substantial fraction of the ammonia in the flushing liquor will be present as ammonium chloride or other fixed ammonia. Alkaline stripping is required to spring fixed ammonia. Modern ammonia stills at coke plants are usually designed for a residual of about 50 mg/l of total ammonia in the still bottoms. A two-stage stripping operation is usually employed with lime or caustic soda being added to the second stage to spring ammonia from strong acid anions.

Some modern stripping processes, such as Chevron in the petroleum industry and Cyam of U. S. Steel, employ controlled pH in the first stage to preferentially separate weak acid gases (HCN, H_2S, and CO_2). The result is improved biological plant effluent quality inasmuch as cyanide is somewhat refractory to biological processes. In addition to the previously mentioned processes, Bethlehem Steel Company[10] has developed a single-stage alkaline stripping process that features low

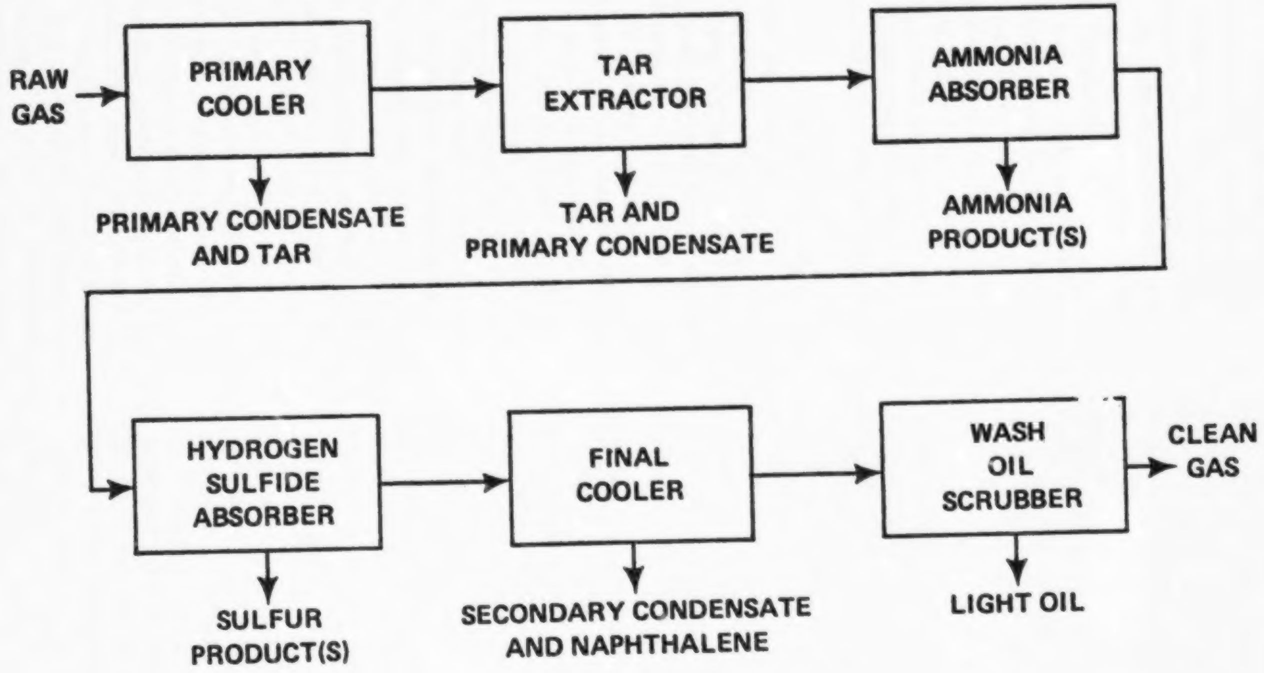
RAW GAS
PRIMARY COOLER
PRIMARY CONDENSATE AND TAR
TAR EXTRACTOR
TAR AND PRIMARY CONDENSATE
AMMONIA ABSORBER
AMMONIA PRODUCT(S)
HYDROGEN SULFIDE ABSORBER
SULFUR PRODUCT(S)
FINAL COOLER
SECONDARY CONDENSATE AND NAPHTHALENE
WASH OIL SCRUBBER
LIGHT OIL
CLEAN GAS

Figure 1. Schematic of coke plant gas purification.

steam consumption and improved ammonia stripping efficiency.

Wastewater Treatment

The present trend at coke plants for wastewater treatment is towards the activated sludge process. The process features remarkable removal of phenol to sub mg/l levels but usually provides somewhat less impressive removal of thiocyanates and cyanides. The limitations of the process include effluent color and occasional inconsistencies in respect to discharge of suspended solids, thiocyanates, and cyanides. Efficient removal of ammonia in the stripping operation will encourage consistent degradation of thiocyanate and cyanide.

Process Performance

The composition of the primary condensates from tar-producing coal gasification processes are basically similar to primary condensates from coke plants operating on similar coal. The gas volume per ton of coal is much larger from gas plants than from coke plants which results in lower concentrations of impurities in the gas and larger units for gas purification. The larger gas volume would also be expected to produce a larger volume of a more dilute primary condensate per ton of coal feed.

The combination of similarity in composition and historical record of similar treatability characteristics should enable the transfer of sufficient gas cleaning and waste treatment technology to justify the substitution of a development study for a much more involved research study. That is, for purposes of experimental design, it can be projected: (a) that a biological process will perform well in the 80 to 95° F range, (b) that pure culture processes are impractical, (c) that the food-to-microorganism ratio will be less than 0.2 lb BOD/lb volatile suspended solids, (d) the yield of cell substance will be from 0.2 to 0.5 lb/lb BOD removed, and (e) that the final clarifier unit solids loading will be from 20 to 30 lb/day = sq ft. It can be further projected that the following concentration ranges will be representative of the settled effluent: (a) suspended solids 60 to 200 mg/l, (b) phenol 0.05 to 0.5 mg/l, (c) thiocyanate 1 to 10 mg/l, (d) cyanide 1 to 10 mg/l, (e) sulfide 0.01 to 0.3 mg/l, and (f) BOD 50 to 150 mg/l. The availability of such guideline information limits the scope of investigative effort and is therefore of great assistance in the design of developmental studies to rapidly verify expected process performance on specific waste flows.

Biological processes are capable of producing a range of effluent qualities. The penalties associated with increased performance are larger aeration units, larger clarification units, and increased energy consumption. Energy consumption is derived primarily from power expended for aeration and agitation of culture — plus heat requirements to maintain acceptable culture temperature in cold weather. It is important that aeration/agitation methodology not adversely affect settleability of the activated sludge culture. Research is indicated to identify optimized design concepts that achieve process objectives at low energy consumption and minimum cost.

Process Development

A vast literature of inconsistent study findings is available to designers of activated sludge processes for coke plants and gas plants. Some degree of rationalization of study findings is sometimes possible by interpretation of literature information within the constraints of process principles. Parenthetically, it should be recognized that coal gas condensates are highly colored and chemically complex so as to pose analytical enigmas. Reported values of biochemical oxygen demand (BOD) may reflect interference due to toxicity. Developmental analytical techniques are recommended for reliable determination of BOD [11]. Chemical oxygen demand tests, using dichromate or permanganate, are subject to interference from chlorides which often are present in abundance. Compensation for chloride interference was tedious prior to modification of the COD test in 1963. The primary condensates contain a host of phenolic substances which may or may not be reported by particular analytical methodology employed in literature studies. Free cyanide will be in equilibrium with metal cyanide complexes and thiocyanate. Therefore, the concentration registered by analysis may depend upon the processing of the sample. Thus, discretion is indicated in the interpretation of literature information. Improved interpretation of previous studies would be possible if reliable correlations between parameters were developed through research.

Most studies of biological treatment of ammonia still wastes have concluded that phosphate is the only mineral nutrient supplement required; whereas some studies advocate addition of phosphate, magnesium, and potassium[12]. Process fundamentals suggest that the waste substrate should supply the microorganisms with the mineral composition required for synthesis of cell substance, possibly similar to the guideline composition given in Table 1. The elements carbon, hydrogen, oxygen, nitrogen, and sulfur are inherently available in adequate quantity with activated sludge treatment of ammonia still waste. The elements phosphorous, sodium, potassium, calcium, magnesium, and iron are normally present in flushing liquor in low concentrations unless opportunity is provided for leaching from gas-borne particulates. Ample calcium is present after stripping in a lime still, but the process effects virtually complete precipitation of magnesium and phosphate. Stripping in a caustic still induces precipitation of calcium and magnesium.

Table 2 presents a hypothetical comparison of approximate quantities of the nutrients present in Synthane coal gasification process condensate and coke plant ammonia still feed, versus bacterial composition from Table 1. The elements contained in Table 2 are of low volatility and therefore tend to report to the char and fines during gasification or coking. The concentration levels in the condensate are presumably dependent upon the degree of leaching from the fines. The coke plant ammonia still feed reflects contributions from Phosam purge and light oil refining as well as flushing liquor. The indicated calcium deficiency would become a surplus if lime were utilized in the ammonia stripping operation. The indicated iron deficiency is generally less at coke plants where higher concentrations of cyanides are present and there is more opportunity for leaching of fines. The difference between the requirement and presence of potassium in the condensate suggests a deficiency, but most coke plant biological treatment processes perform well without supplemental potassium nutrient. It is conceivable that at coke plants potassium is leached from fines or present in other feeds connected to the biological plant.

TABLE 1

REPRESENTATIVE ELEMENTAL COMPOSITION OF DRY BACTERIAL PROTOPLASM

	Wt.%		Wt.%
C	50	Na	0.7
H	5.8	K	0.5
O	27	Ca	0.7
N	12	Mg	0.5
P	2.5	Fe	0.1
S	0.7		

Adapted from: R. E. McKinney (13)

To date, biological treatment of coke and gas plant wastes has been characterized by limited process stability. Until such occasional problems are resolved. the possible role of trace nutrients should be kept under consideration—especially in view of the variability in coal feeds and the importance of magnesium as an enzyme constituent. Most studies have indicated that phosphate is the only nutrient addition required for biological treatment of wastewater from coke and gas plants, but high efficiency ammonia stripping may lower residuals of magnesium and calcium (caustic stills) and revisions in gas cleaning may reduce the opportunity for leaching from gas-borne particulates. Lower gas cyanide levels could also limit the leaching of metals from particulates. Nutrient requirements for biological processes can be evaluated relatively simply by experimental procedures involving several culture transfers in developmental type determinations of BOD rates[11]. Such evaluations are recommended on a case-by-case basis pending resolution of the question.

Dilution of wastewater is sometimes advocated for biological treatment of coke plant wastes. Dilution will lower the exposure of the microorganisms to refractory substances such

TABLE 2

HYPOTHETICAL COMPARISON OF TRACE NUTRIENT COMPOSITION VS. INDICATED BACTERIAL REQUIREMENT FOR SYNTHANE CONDENSATE AND COKE PLANT AMMONIA STILL FEED

	Indicated Requirement lb/1,000 tons	Synthane Condensate[a] Indicated Present lb/1,000 tons	Still Feed Indicated Present lb/1,000 tons
Ca	10	5.1	5.9
Fe	2.8	0.28	3.2
K	14	0.78	16
Mg	14	1.6	3.5
Na	20	19	95
P	70	0.12	57

[a] Illinois #6 Coal, Forney, A. J. et al. (14).

as salts and hard organics, but in the completely mixed activated sludge process, degradable substances are present at effluent concentration levels—suggesting minimum justification for dilution. Dilution can assist in the control of calcium sulfate precipitation resulting from reaction between residual calcium from lime stills and sulfate formed during aeration by biooxidation of thiocyanate and reduced sulfur compounds.

Effluent Polishing

High dissolved solids in the feed to activated sludge processes has been associated with increased effluent suspended solids. In addition, the culture of activated sludge systems sometimes loses its ability to settle which results in increased discharge of suspended solids with the effluent. Such periods are sometimes termed "upsets." However, if the process is viewed as operating in dynamic equilibrium rather than in steady state, it is conceivable that periods of loss of culture settleability could be a part of the normal spectrum of operations. In any event, the discharge of excess suspended solids is often difficult, and sometimes impossible, to correct by adjustment of plant operational practices. The implementation of effluent polishing may be required to achieve effluent suspended solids levels associated with domestic sewage activated sludge plants. Granular media filtration has been employed for effluent polishing, but lamella dissolved air flotation has been demonstrated as superior for the capture of significant overages of suspended solids[15]. The flotation process was capable of clarifying feeds with 300 mg/l suspended solids to the 25 to 35 mg/l range. Dissolved air flotation was also advantageous in that the captured solids are collected in a low volume float instead of a large volume backwash.

Research Trends

Preliminary absorption of halides is a concept that has potential for improving water management of coal conversion processes. The concept, illustrated in Figure 2, features a controlled temperature—controlled volume scrubbing operation followed by demisting to capture strong acid salts in a low volume purge. The asset of the concept is that subsequent condensates are low in strong acid salts and therefore more applicable to incorporation in recycle circuits. The low volume characteristic of the purge concentrate will facilitate disposal

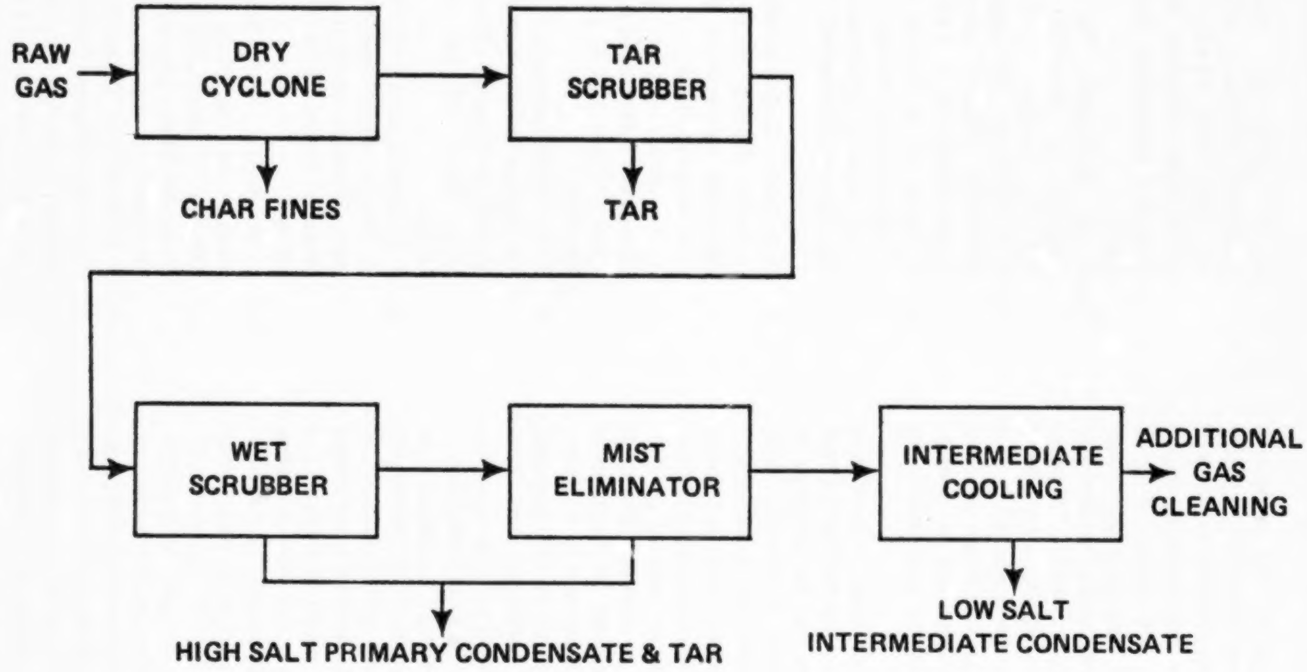
RAW GAS
DRY CYCLONE
CHAR FINES
TAR SCRUBBER
TAR
WET SCRUBBER
MIST ELIMINATOR
HIGH SALT PRIMARY CONDENSATE & TAR
INTERMEDIATE COOLING
LOW SALT INTERMEDIATE CONDENSATE
ADDITIONAL GAS CLEANING

Figure 2. Schematic of preliminary absorption of halides.

or recovery, but the fate of the concentrate is an unresolved aspect of the concept.

SUMMARY AND CONCLUSIONS

Modern coke plants provide fuel gas that is highly acceptable for many industrial purposes. Prior to use, the gas is processed for removal of particulates, naphthalene, ammonia, hydrogen sulfide, and light oils. The proven process technology employed for coke oven gas cleaning is adaptable to the cleaning of cooled producer gas for industrial consumption, but process revisions would be required for the cleaning of substitute natural gas. On a per ton of coal basis, larger volumes of gas and larger volumes of a more dilute condensate will be derived from producer gas operations than from coke plant operations.

The activated sludge process is commonly employed for wastewater treatment at modern coke plants. The process can be designed to provide excellent removal of phenol, thiocyanate, BOD, and cyanide. The limitations of activated sludge treatment of coke plant waste are dark color in the effluent and occasional inconsistencies in performance relative to thiocyanates, cyanides, and suspended solids. Effluent polishing by dissolved air flotation is worthy of consideration inasmuch as the process is better able to handle slugs of suspended solids than filters. In addition, the float separated from the flotation process is a concentrate rather than a dilute filter backwash.

Activated sludge technology is adaptable to treatment of condensates from tar producing coal conversion processes. The application of the data base available from coke plant waste treatment will reduce a research project to a developmental project at a vast saving in time and effort. Coal condensates may be deficient in trace element nutrients such as magnesium and potassium. Evaluation of nutrient adequacy is recommended as part of developmental studies. The nutrient situation may differ depending upon the efficiency of processes for the removal of particulates and ammonia.

Preliminary absorption of halides is a concept that has potential for improving water management at coal gasification facilities. The separation of a low volume, high salt concentrate would reduce disposal problems and increase the feasibility of water reuse.

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FUTURE NEED AND IMPACT ON THE PARTICULATE CONTROL EQUIPMENT INDUSTRY DUE TO SYNTHETIC FUELS

John Bush
Research-Cottrell, Inc.
Bound Brook, New Jersey 08805

Abstract

The growing demand for coal conversion processes requires a concurrent assessment of the equipment and systems needed for the control of discharge pollutants entering the environment. The particulate control equipment industry will be affected by the increased coal consumption, by the advanced processes being developed, and by the limitations of existing collection systems. This paper presents an extrapolation of the total energy growth in the United States, its impact for coal consumption, and the need for particulate control in each process. Process control conditions are examined to show whether existing equipment designs are adequate and to show where new and developing designs are needed. The future presents a continuing demand for particulate control with greater emphasis on fine particulate collection and with new control conditions for the advanced coal processes that are expected to be commercialized by 1985.

INTRODUCTION

Energy consumption within the United States has been increasing at a rapid growth rate, and is expected to continue in the near future at the same pace. By the year 2000, following this extrapolated growth rate, the total energy consumption[1] will be double that amount presently used during 1976 (Table 1). This increase in energy demand can only be met through increased coal production and through construction of nuclear energy plants. The coal production required for a doubling of energy will be a three-fold level above current production, increasing from 13.5 quadrillion Btu to a new level of 52 quadrillion Btu in 2000. This production and use of coal could result in substantial environmental damage, unless control technology is developed and applied now for each developing coal process.

TABLE 1

ENERGY USE BY SOURCE (10^{15} Btu)$^{(1)}$

	1976	2000
Petroleum	34.9	55
Natural Gas	20.2	
Coal	13.6	52
Nuclear	2.1	34
Hydro	3.0	3
Other	----	6
TOTAL	73.8	150

Coal conversion processes are being directed along three major routes: (1) combustion to produce heat and electricity; (2) gasification which can result in either a high Btu synthetic natural gas or in a low Btu producer gas for nearby industrial use or for combined cycle electrical generating; and (3) liquefaction to produce oil and chemical feedstocks as a supplement to diminishing supplies of petroleum resources. Immediate production will emphasize combustion systems using available burners and boiler systems. Following technical development and environmental assessment through 1985, advanced combustion systems will be built, with a lesser impact due to the gasification and liquefaction processes. All of these processes will require particulate emission control and gaseous emission control, with the degree of control specified by each individual conversion process and operating conditions.

For any process the selection of a control system must be based first on feasibility and finally on economics. This selection procedure (Figure 1) has three steps: (1) knowledge of regulated emission levels and the amount and type of pollutants present to be controlled; (2) a description of all process streams with total characterization of gas and particulate; and (3) design choice alternatives for each particulate control system. The emission standards are established by Federal and State regulatory agencies based on possible health and ecological effects in the environment for each

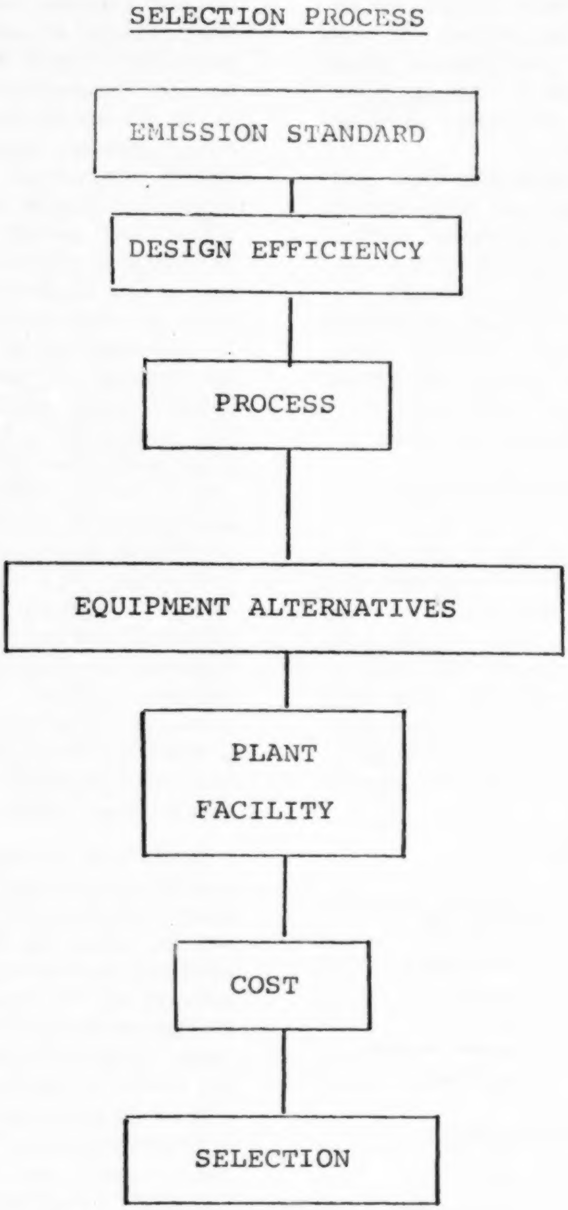
SELECTION PROCESS
EMISSION STANDARD
DESIGN EFFICIENCY
PROCESS
EQUIPMENT ALTERNATIVES
PLANT
FACILITY
COST
SELECTION

Figure 1. Particulate control equipment selection procedure.

individual pollutant. Each coal conversion process has different designs, different operating characteristics and different control locations depending on downstream process equipment and products. In each stream the gas and particulate need to be characterized for their physical and chemical properties—a partial listing is included in Table 2—that can affect collection mechanisms and design specifications for a control system.

Using the detailed characterizations, each alternative control system can be evaluated, first, for a practical operating design, second, for plant facility limitations of heat recovery, waste treatment, space, water availability, product recovery, and third for total costs based on capital expenditures, power costs, maintenance, and waste disposal. Using these final costs a comparison of each control alternative and a final selection can be made.

COAL CONVERSION PROCESSES

Looking now at the individual processes, the particulate control operating conditions and design requirements can be evaluated for those ranges where existing designs may be sufficient and those where new designs must be developed. Coal combustion has three major process systems (Figure 2A): (1) direct combustion of pulverized coal in a conventional utility or industrial boiler; (2) atmospheric fluidized bed combustion; and (3) pressurized fluidized bed combustion. The utility and industrial boiler designs are commercially available and use "conventional" stack-gas cleaning systems. Particulate control systems have operated at gas conditions ranging between 250° F and 800° F to collect fly ash particulate. Temperature varies with the location in the process stream. Major design changes reflect increased requirements for "fine" particulate removal and for cost reductions. Atmospheric fluidized bed combustion produces higher heat transfer coefficients for steam generation and provides for SO_2 removal in the reactor bed. Particulate removal will occur in a stack gas clean-up system, similar to that used for pulverized coal boilers. Emphasis for design requirements is placed on the different particulate characterization. Pressurized fluidized bed combustion is being developed for combined cycle power generation utilizing a gas turbine on the outlet gases. In this process, which is expected for commercialization after 1985, particulate collection must occur ahead of the gas turbine, thus protecting the blades from erosion by large particulate and from attack by the higher alkali content of the fine particulate. Operating conditions for particulate removal will occur between 1500° F and 2200° F at pressures above 10 atmospheres. This is a new process operating range and will require extensive development of control technology as the process advances towards commercialization.

TABLE 2

PARTICULATE CHARACTERISTICS	
Ignition Point	Grain Loading
Size Distribution	Density
Abrasiveness	Shape
Hygroscopic Nature	Physical Properties
Electrical Properties	Explosiveness
GAS STREAM CHARACTERISTICS	
Volume	Odor
Temperature	Explosiveness
Pressure	Viscosity
Moisture	Ionic Mobility
Corrosiveness	Thermal Conductivity
Composition	

Gasification of coal (Figure 2B) is needed to produce a clean fuel gas. The high Btu processes manufacture a synthetic natural gas that will be piped via the existing natural gas pipeline to individual customers. In this process with the gas at a pressure of 1000 psi, particulate removal will occur prior to the catalytic steps ugrading the gas. Operating temperature are currently planned between 200° F and 800° F for particulate removal, with the higher temperatures above 500° F preferred for solid char removal and the lower temperatures 200-500° F required for tar mist removal. The development of catalysts and acid-gas removal systems that could operate at higher temperatures would change the temperature level required for particulate removal. Commercial high Btu gasification will not make a major

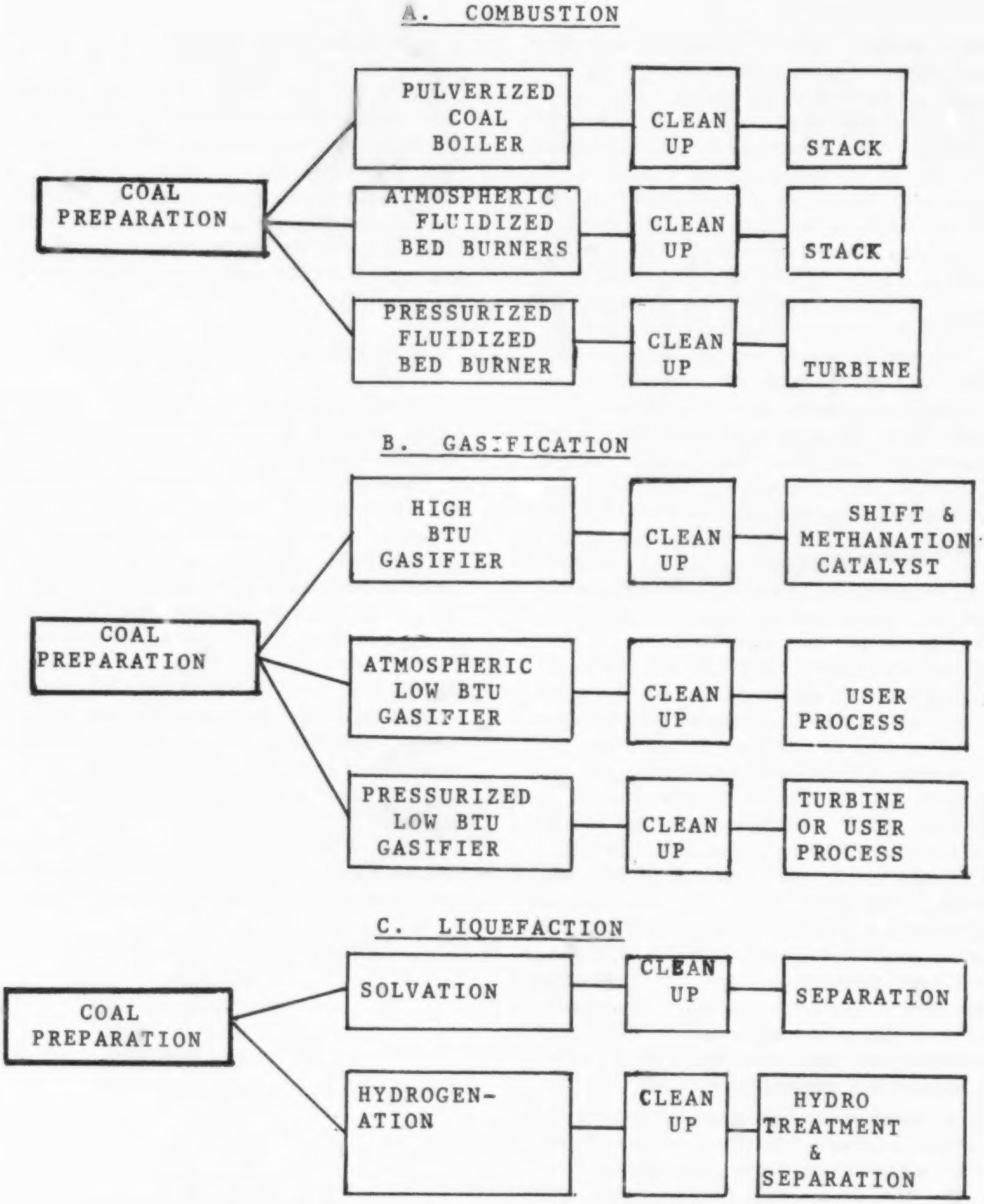
A. COMBUSTION
COAL PREPARATION
PULVERIZED COAL BOILER
CLEAN UP
STACK
ATMOSPHERIC FLUIDIZED BED BURNERS
CLEAN UP
STACK
PRESSURIZED FLUIDIZED BED BURNER
CLEAN UP
TURBINE
B. GASIFICATION
COAL PREPARATION
HIGH BTU GASIFIER
CLEAN UP
SHIFT & METHANATION CATALYST
ATMOSPHERIC LOW BTU GASIFIER
CLEAN UP
USER PROCESS
PRESSURIZED LOW BTU GASIFIER
CLEAN UP
TURBINE OR USER PROCESS
C. LIQUEFACTION
COAL PREPARATION
SOLVATION
CLEAN UP
SEPARATION
HYDROGEN-ATION
CLEAN UP
HYDRO TREATMENT & SEPARATION

Figure 2. Coal conversion processes.

impact before 1984. Atmospheric low Btu gasification, a second process type, is expected to develop more rapidly, with some commercial designs already in use in Europe and Africa. For this process the gas is cleaned and sent to a nearby industrial process or boiler, with the degree of clean-up determined from the end use requirements. Temperatures for clean-up will range from 200-500° F for tar droplets to 500-1100° F for char removal. Particulate collection systems are commercially available for the low temperature range and can be extended to the higher temperatures with advanced material selection. Pressurized low Btu gasification will be used (1) to either supply more distant industrial users in a local pipeline network or (2) in combined cycle power generation. For the former end use, particulate clean-up will occur at pressures from 10 to 30 atmospheres and for a temperature range between 100° F and 600° F. For the combined cycle system entering a combuster and gas turbine, particulate removal under the same high pressure must be performed at higher temperatures above 1200° F. The maximum temperature will be controlled by the combustor inlet conditions to prevent auto-ignition.

Coal liquefaction (Figure 2C) follows two processes: (1) solvent extraction and (2) catalytic hydrogenation. In the former, a hydrogen donor solvent extracts the smaller coal molecules producing a variety of tars, oils, and gases and leaves a residue of char and minerals. The gases, tars, and oils must be separated and cleaned, usually under pressure and at temperatures below 400° F. In the second hydrogenation reaction, the larger coal molecules are split into smaller molecules producing a higher concentration of lighter oils. Purification and separation again occurs under pressure at low temperatures.

In all of the above processes, particulate collection is required in the main gas stream. In addition, secondary streams from residue combustion, regeneration processes, and coal preparation steps will require particulate control. Conditions found in the secondary streams are generally similar to the established process conditions with some variation in temperatures or pressures. Commercially available equipment with extended temperature limits and improved performance designs will meet the requirements for atmospheric pressure coal systems currently preparing for commercialization. New designs and development are needed for the higher temperature (500 to 2000° F) and pressure (10-70 atm) collection requirements found with pressurized fluidized bed combustion, pressurized low Btu gasification, and high Btu gasification processes that are expected to be ready for commercialization by ~ 1985.

PARTICLE CONTROL EQUIPMENT

Having examined the general operating characteristics of the coal conversion processes, the particulate equipment to meet these conditions can now be described. Particulate control equipment choices fall into four major classes (Figure 3): mechanical collectors, wet collectors, filters, and electrostatic precipitators. Each of these classes have existing commercial designs and developing designs to meet the coal conversion process requirements. New designs combining mechanical, wet scrubbing, and electrostatic mechanisms are being studied for fine particulate collection and evaluated to reduce size and cost of an individual system.

Mechanical collectors usually consist of cyclones or centrifuges which can be connected in a series arrangement to attain higher efficiencies. This class of collectors is limited to the collection of particles larger than 5

MECHANICAL COLLECTORS

CYCLONES
CENTRIFUGES

WET COLLECTORS

SCRUBBERS

FILTERS

BAGHOUSES
GRANULAR BED FILTERS

ELECTROSTATIC PRECIPITATORS

Figure 3. Particulate control equipment alternatives.

microns, and is generally used for a first stage as a precollector of large particulate. Mechanical collectors can be designed for essentially all of the temperatures and pressures found in coal conversion.

Wet collectors such as scrubbers or wet electrostatic precipitators can effectively collect particulate at low temperatures. Both scrubbers and precipitators have been applied at high pressures to 60 atmospheres in past commercial designs. Consideration must be given to the need and cost of additional waste water treatment when applying these systems. Temperature is a limiting factor for the liquid being used as the spray or scrubbing media, in that the gas must be saturated for efficient operation with condensing droplets.

Filters operate by particulate collection on fibers or granular beds. Baghouses consisting of woven fabrics have operated at essentially atmospheric pressure with temperatures ranging to 550° F on industrial boilers and recently on utilities. Material bag life is presently limited in use to the temperatures below 600° F. Granular bed filters and panel bed filters are new designs developed primarily for high temperature and pressure applications. These filters collect fine particulate by building a "filter cake" from the collected particulate onto the granular bed. High pressure drops have usually been found with these systems.

Electrostatic precipitators (wet or dry) have long been in use for efficient collection of tar and various types of dust in both industrial and utility applications. New designs being funded by industry, EPA, and utilities are aimed at improving performance and reducing costs—both capital and operational. Past experiences in precipitation have found applications for atmospheric systems from 200 to 900° F and for high pressure systems from 1 to 60 atm at temperatures generally below 300° F.

Operating data is limited for each of the above classes at the combined high temperature and pressure needed for the developing coal process conditions that exceed existing control ranges. Several companies under contract to EPA and ERDA are developing new designs and concepts for high temperature and pressure particulate removal. Consolidated Coal Company and Mechanical Technology, Inc., are developing high efficiency cyclones using a high pressure drop that collects particulate above 5 microns. Series of three to four cyclones are expected to be required to attain high collection performance. Gravel bed or panel bed systems are being developed and evaluated by Rexnord, Inc., Duccon (used at Exxon's miniplant), Air Pollution Technology, Inc., and Combustion Power Company. Acurex Corporation/Aerortherm is developing a ceramic bag filter for use at high temperature and pressure. Westinghouse is evaluating a ceramic membrane filter under similar conditions. Air Pollution Technology is evaluating a scrubber to be used at high pressures and moderately high temperatures. Research-Cottrell is developing high temperature and pressure electrostatic precipitators for use under all expected operating conditions. Each developing control system is being evaluated under laboratory and pilot operation. Currently, performance predictions and design criteria are poor or lacking at these high temperatures and pressures. Both gaseous and particulate characteristics are essentially unknown. Pilot and demonstration scale systems are needed to provide reliable design data and material selection for long life on all new particulate equipment. At high temperatures, the efficiency of all control equipment for any given size can be expected to decrease due to the increasing value of the gas viscosity; however, electrostatic precipitators are unique in their collection mechanism in that the migration velocity and thus efficiency increases with an increasing applied voltage. Research-Cottrell is conducting a precipitator program evaluating conditions to 500 psi and to 2000° F in air, combustion gas, and a simulated fuel gas. These results have found precipitation to be very favorable for the higher gas densities found with high pressures that maintain substantially higher applied voltages. These higher voltages are capable of increasing precipitator efficiency and reducing its size and cost. Corona current was stable in all gas mixtures evaluated.

FUTURE IMPACT

Advanced designs and future control requirements are evolving towards a higher collection efficiency of fine particulate, minimal energy consumption, control ranges at a variety of temperatures and pressures, and the capability of handling changing particulate properties due to variations in chemical composition and operating conditions. Catalytic steps and turbine operation require clean-up locations at the higher temperatures and pressures leaving the coal conversion reactor.

Comparative performance evaluation combined with capital investment, operating costs, and maintenance will ultimately determine a final control choice for any one process. The varying process conditions will result in control equipment systems being designed for specific operating conditions, based on economics and collection mechanisms.

In summary, coal conversion processes will continue to require particulate removal, with the particulate control equipment industry growing at approximately the same pace as coal use. Advanced developments requiring high temperature and pressure particulate removal will become commercialized around 1985. Atmospheric combustion processes in utilities and industry will continue to grow prior to that time. Each new design concept will be required to efficiently remove fine particulate under the given process conditions. New design and process optimization between control system and conversion process will be required to minimize costs and improve performance. Particulate control development must occur now with the developing advanced coal conversion processes if commercialization is to be achieved at a minimal cost by 1985.

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FUTURE NEEDS AND THE IMPACT ON THE WATER AND WASTE EQUIPMENT MANUFACTURING INDUSTRY DUE TO THE USE OF SYNTHETIC FUELS

E. G. Kominek, P.E.
Technical Director, Water and Waste
Envirotech Process Equipment Division
Envirotech Corporation
Salt Lake City, Utah

Probably the most important needs of the water pollution control equipment industry are coal conversion wastewater characterizations which can be used more specifically for the design of chemical and/or biological waste treatment systems. These should include analyses which differentiate between organics which are readily biodegradable, as indicated by BOD_5 analysis, slowly biodegradable compounds which report as BOD_{20} and COD or TOC determinations which would indicate by difference the approximate concentration of nonbiodegradable organic compounds.

Total Kjeldahl nitrogen determinations would also be important for consideration of nitrification—and possibly denitrification of plant effluents in the waste treatment plant designs. Whenever possible, cell yield coefficients and endogenous rate coefficients should be determined so that food/microorganism ratios and sludge ages can be correlated for activated sludge aeration basin design calculations. Treatability factors for contact media unit design would also be helpful for evaluation purposes.

If laboratory facilities are available at pilot plant installations, biological treatability tests, including nitrification, should be made. Denitrification studies would also have long-range benefits. There are many cyclic organics and metal salts which may interfere with nitrification or denitrification and it may be necessary to pretreat to remove metal salts, or to feed powdered activated carbon into the biosystems to adsorb organics which could interfere with the biological processes.

The DuPont Waste Treatment Plant at their Chambers Works in New Jersey and the API study recently made at the Texaco plant, Port Arthur, Texas, have demonstrated the benefits of powdered activated carbon in activated sludge systems treating organic chemical wastes and petroleum-petrochemical wastes. This may also be true of coal gasification and liquefaction wastewaters.

The evaluation of biosystem plant design must take into consideration the potentially toxic effect of high concentrations of chemicals resulting from spills or upsets in the plant operations. The recovery time of a biosystem can be long—so this is an important operational consideration.

The need for surge and also backup treatment units must be evaluated for each system being considered. Before going into final design, pilot plant tests under the worst conditions which can be anticipated may indicate a preferred waste treatment process.

Biological sludge disposal can be an important factor. Excess biological sludge production varies appreciably. With 30-day sludge age and temperature of 10° C-30° C, it will range from 0.3 to 0.4[1] lbs of sludge being produced per lb. of BOD removed. The biosludge can only be concentrated to about 3 percent to 4 percent without filtration—so the volume is appreciable.

It would be to ERDA's advantage to investigate:

- Anaerobic treatment of strong wastes
- Aerobic treatment using contract media and activated sludge
  - With atmospheric oxygen
  - With pure oxygen
- Wet air oxidation of strong wastes
- Backup facilities required to handle upsets.
  - This should include granular activated carbon and reverse osmosis as polishing operations.

Characterizations of inorganic wastes are also important. Segregation of inorganic wastes can simplify treatment and save money. Most heavy metals in cationic form will precipitate to very low residual concentration as hydroxides or sulfides. Chemical treatment will release and allow precipitation of metal complexes, at least when treating waste solutions from boiler-cleaning operations.

Cooling tower blow-down can be minimized by appropriate makeup water of sidestream treatment. In many cases, the silica concentration of the cooling water determines required blow-down. It would help to have complete mineral analysis of the raw waters and knowledge of the planned cycles of concentration for optimizing the design of cooling systems to reduce blow-down.

Spent ion exchange regenerants in boiler blow-down should be kept out of the wastestreams which require biological treatment. The systems can be designed for partial recovery of ion exchange regenerants and rinse waters, thereby reducing the wastewater effluent volume.

As gasification and liquefaction processes become more refined, evaluations of water and waste treatment methods under comparable conditions will help in selecting the most cost effective methods based upon capital cost and energy requirements. They will also provide reasonable assurance of reliable operations under the varying wastewater characteristics from gasification or liquefaction plant operations which are inevitable.

And now, for a discussion of the projected impact of the synthetic fuels industry on the water pollution control equipment industry. The production of synthetic fuels will have an impact. However, it appears at this time that any major effects of coal conversions will not be felt until the mid-1980's or later. Current coal conversion processes are directed toward pilot plant or demonstration plant testing. Apparently this will continue until about 1980. According to ERDA's F'78 Fossil Energy Research Program[1], there are ten coal liquefaction, five pyrolysis, eight high Btu coal gasification, and nine low Btu coal gasification projects budgeted for further tests. ERDA's budget projects an increase from about $350 million in F'77 to $448 million in F'78 to maintain the coal program. $53 million in expenditures are projected for demonstration plants in F'77—and only $50 million, in F'78.

The Fossil Energy Coal Program has five categories of projects:

1. Laboratory bench-scale
2. Process development units
3. Pilot plants
4. Demonstration plants
5. Commercial demonstration plants

The only two which will involve significant expenditures for liquid waste treatment are:

- Demonstration plants operating a single modular unit using commercial sized components to demonstrate and validate economic environmental and production parameters;
- Commercial demonstration plants to establish actual economic factors and environmental feasibility. These will be three to five times the capacity of demonstration plants by combining modular production units.

The larger installations projected include the H Coal Direct Hydrogenation Process Pilot Plant at Ashland Synthetic Fuels, Catlettsburg, Kentucky. This plant has a coal input of 600 TPD. It is in the procurement and construction stage and operation is projected through the third quarter of F'80.

The Solvent Refined Coal Liquefaction Process, budgeted at $16 million in F'78 includes a pilot plant with a capacity of 50 TPD coal at Pittsburgh and Midway Coal Mining, Ft. Lewis, Washington.

The Donor Solvent Liquefaction Process budget is scheduled for $30.3 million in F'78. Exxon Research and Engineering, Baytown, Texas, will operate a process development unit through the third quarter of F'81. A pilot plant is scheduled for design and construction over a 2.5-year program in operation from F'80 through three quarters of F'81.

The major budgets for High Btu Gasification Processes are:

Bi-Gas - 120 TPD coal pilot plant, Bituminous Coal Research, Homer City, Pennsylvania. Pilot plant operation scheduled through third quarter F'79.

Synthane - 75 TPD coal pilot plant, Pittsburgh Energy Research Center, Pittsburgh, Pennsylvania. Operation scheduled through middle of F'79.

Hy-Gas - 80 TPD pilot plant, Institute of Gas Technology, Chicago, Illinois. Project evaluation by end of F'79.

CO_2
Acceptor - 40 TPD coal pilot plant, Consolidation Coal/Conoco Coal Development, Rapid City, South Dakota. Project evaluation by end of F'79.

The major budgets for Low Btu Gasification Projects are:

Lurgi combined cycle test facility for Commonwealth Edison at Pekin, Illinois, capacity 480 TPD coal. The plant is to operate through F'82.

Hydrogen from coal facility, capacity 200 TPD coal is projected to operate from F'81 for about three years.

Combustion Engineering, Windsor, Connecticut, has a 120 TPD atmospheric entrained bed gasification unit in operation. It is scheduled for evaluation in F'79.

R. Antonsen[2], Assistant Program Director, Division of Major Facility Program Management of the ERDA, has reported that:

> "Two pipeline gas projects are in the conceptual design phase. It is estimated that an evaluation of the two projects will be made in about June 1978. The estimated input of one of the projects is 3800 TPD of coal.
>
> The other project involves a conceptual design of a pipeline gas plant using the IGT Hy-Gas Process. This is projected to use 7500 TPD of coal.
>
> A fuel gas project under consideration plans to use 2800 TPD of coal. Another involves 2270 TPD of coal.
>
> An atmospheric fluidized bed combustion unit is planned using 1600 TPD of coal.
>
> A solvent-refined coal project is projected using 600 TPD of coal."

It is significant that several contractors had submitted proposals for demonstration plants in 1976. However, as of July 1977, these proposals were still being evaluated.

ERDA's Office of Commercial Applications advised that any projects which require financial assistance from the Federal government would need funds voted by Congress after review and approval by the Department of Energy. There apparently are not commercial size gasification or liquefaction projects that are being prepared for presentation to Congress for funding in F'78. It would appear that unless projects are funded by industry, the processes currently being publicized will have to go through the demonstration plant stage with ERDA assistance before full-scale plants are considered.

Pilot plant or demonstration plants in the 400 to 600 TPD coal capacity range would probably have commercial scale water and waste treatment plants. The others would be more or less in the pilot waste treatment category. It therefore does not seem likely that the United States will be far beyond the commercial demonstration plant stage before 1985 unless an international crisis or the need for a major project to stimulate the U.S. economy, or a program to reduce an unfavorable trade balance through and accelerated synthetic fuel program, changes the priorities.

But, if we ignore the question of "when," the following provides some indication of the potential long-range impact of the water and waste treatment needs of coal gasification and liquefaction plants.

C. F. Braun made a comprehensive study which is detailed in the Interim Report, "Factored Estimates for Western Coal Commercial Concepts"[3], prepared for ERDA and the American Gas Association. This report was published in October 1976. These plants were evaluated on a comparable basis, with coal consumptions of approximately 8 million tons/year per plant, each with a capacity to produce about 250 million cubic feet/day of synthetic gas.

Coal gasification plants use considerable water. Table 1[4] lists the estimated water requirements for a Lurgi Process plant processing 21,800 TPD of coal. Based upon 5100 gpm input, 79.8 percent of the water is consumed in proccess or is lost by evaporation. The makeup water requirements of the six processes vary as shown on Table 2. Note that the estimated raw water usage of the six systems range from about 114,000 to 203,000 GPH.

Table 3 shows the estimated water treatment costs, ranging from $285,000 to $580,000, to clarify or lime-soften the makeup water. Granular media filtration and

TABLE 1

WATER REQUIREMENTS AND DISPOSITION OF A LURGI COAL GASIFICATION PLANT PROCESSING 21,800 TPD OF COAL

	GPM	%
PROCESS CONSUMPTION		
TO SUPPLY HYDROGEN	1,120	
PRODUCED AS METHANATION BYPRODUCT	-600	
NET CONSUMPTION	520	10.2
RETURN TO ATMOSPHERE		
EVAPORATION:		
FROM RAW WATER PONDS	420	
FROM COOLING TOWER	1,760	
FROM QUENCHING HOT ASH	150	
FROM PELLETIZING SULFUR	250	
FROM WETTING OF MINE ROADS	730	
	3,310	
VIA STACK GASES(1):		
FROM STEAM BLOWING OF BOILER TUBES	200	
FROM STACK GAS SO_2 SCRUBBERS	40	
TOTAL RETURN TO ATMOSPHERE	3,350	69.6
DISPOSAL TO MINE RECLAMATION		
IN WATER TREATING SLUDGES	100	
IN WETTED BOILER ASH	30	
IN WETTED GASIFIER ASH	300	
TOTAL DISPOSAL TO MINE	430	8.4
OTHERS		
RETAINED IN SLURRY POND	20	
MISCELLANEOUS MINE USES	580	
TOTAL OTHERS	600	11.8
GRAND TOTAL	5,100	100.0

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(1) DOES NOT INCLUDE WATER DERIVED FROM BURNING OF BOILER FUEL

TABLE 2

PROCESS	RAW WATER GPH
IGT STEAM OXYGEN HY-GAS	114,000
IGT STEAM IRON HY-GAS	203,000
CONOCO CO_2 ACCEPTOR	136,000
BCR BI-GAS	129,000
PERC SYNTHANE	150,000
LURGI	146,000

demineralization equipment was estimated to range from $709,000 to $2,450,000. Adding the estimated costs for deaeration equipment, sodium exchange for low pressure boilers and ion exchange equipment for condensate polishing, the estimated equipment cost ranged from $1,742,000 to $3,335,580. The estimated installed costs ranged from $3.5 to $6.7 million.

It has been predicted that two SNG coal-based plants will be in operation and producing 0.16 x 10^{15} Btu per year by 1985[5]. Another forecast indicates 0.4 x 10^{15} Btu per year, which would indicate the need for five plants, each processing 8 million tons of coal/year. If we assume that the water treatment equipment for these plants would be purchased in 1981 or 1982, the estimated cost of the water treatment equipment in 1977 dollars would be in the range from $3.5 to $6.7 million for two plants and $8.5 to $17 million for five plants.

Table 4 compares the costs of waste treatment equipment and auxiliaries for the six processes studied by Braun. The estimated cost of equipment for chemical coagulation, flotation to remove tars and oils and staged activated sludge treatment, together with aerobic digestion, thickening and vacuum filtration of waste sludge would range from about $2.6 to $5.3 million per plant. With pumps and tanks added, the estimates range from about $3 to $6.1 million. Estimated installed costs assume that the civil works would be about 80 percent of the total costs—or in the range from $15.3 to $30.5 million.

The estimates are all based upon the use of western coal. The type of coal used would have a significant effect upon the wastewater analyses as shown in Table 5[6]. However, as there are many other variables which would influence the cost of waste treatment plants at the time when they are considered for final design, any closer estimates would have to be made on a case by case basis, using the latest technologies for coal conversion and for waste treatment.

It is assumed that on a comparable coal tonnage basis, the wastewater from coal liquefaction processes would have about the same pollution load as the coal gasification projects and that the treatment costs would be in the same order of magnitude. The estimation of either two or five plants by 1985 would have a moderate impact. However, the water and waste treatment equipment manufacturing industry should be operating at a high level in the early 1980's because of equipment expenditures for compliance with the EPA's BAT standards which are scheduled to go into effect in 1983. As the present guidelines will probably be supplemented by additional standards for compliance with the Toxic Substances Control Act, the impact of an additional $6 million to $30 million in waste treatment equipment and appurtenances for coal conversion plants would not be significant.

TABLE 3

WATER TREATMENT

	IGT STEAM OXYGEN HYGAS	IGT STEAM IRON HYGAS	CONOCO CO_2 ACCEPTOR	BCR BIGAS	PERC SYNTHANE	LURGI
DRY COAL TO PROCESS TONS/HR	568	742	699	578	929	632
RAW WATER GAL/HR	114,000	203,000	136,000	129,000	150,000	146,000
LIME SOFTENING - CLARIFICATION	$ 285,000	580,000	330,000	350,000	345,000	435,000
FILTERS AND DEMINERALIZERS	980,000	2,450,000	1,470,000	1,310,000	790,000	900,000
DEAERATORS	212,000	295,000	185,000	330,000	420,000	255,000
SODIUM EXCHANGERS	105,000	340,000	--	290,000	340,000	510,000
CONDENSATE POLISHERS	160,000	250,000	220,000	350,000	--	--
TOTAL	$1,742,000	3,335,580	2,205,000	2,630,000	1,895,000	2,100,000
ESTIMATED INSTALLED COSTS	$3,500,000	6,700,000	4,400,000	5,300,000	3,800,000	4,200,000

TABLE 4

WASTEWATER TREATMENT

	IGT STEAM OXYGEN HYGAS	IGT STEAM IRON HYGAS	CONOCO CO_2 ACCEPTOR	BCR BIGAS	PERC SYNTHANE	LURGI
DRY COAL TO PROCESS TONS/HR	568	742	699	578	929	632
RAW WATER GAL/HR	114,000	203,000	136,000	129,000	150,000	146,000
ORGANICS REMOVED BY BIOLOGICAL TREATMENT LBS/HR	6,600	8,000	--	--	5,100	1,200
EQUIPMENT	$ 3,992,000	5,311,000			3,305,000	2,631,000
TANKS	382,000	507,000			285,000	288,000
PUMPS	150,000	283,000			146,000	150,000
TOTAL	$ 4,524,000	6,101,000			3,736,000	3,069,000
ESTIMATED INSTALLED COST	$22,620,000	30,505,000			18,680,000	15,345,000
WASTEWATER EVAPORATORS	$ 5,800,000	15,000,000	6,400,000	9,800,000	8,100,000	8,800,000

TABLE 5

BYPRODUCT WATER ANALYSIS FROM SYNTHANE GASIFICATION OF VARIOUS COALS, MG/L (EXCEPT pH)

	COKE PLANT	ILLINOIS NO. 6 COAL	WYOMING SUBBI-TUMI-NOUS COAL	ILLI-NOIS CHAR	NORTH DAKOTA LIGNITE	WESTERN KENTUCKY COAL	PITTS-BURGH SEAM COAL
pH..............	9	8.6	8.7	7.9	9.2	8.9	9.3
SUSPENDED SOLIDS	50	600	140	24	64	55	23
PHENOL..........	2,000	2,600	6,000	200	6,600	3,700	1,700
COD.............	7,000	15,000	43,000	1,700	38,000	19,000	19,000
THIOCYANATE.....	1,000	152	23	21	22	200	188
CYANIDE.........	100	0.6	0.23	0.1	0.1	0.5	0.6
NH_3.............	5,000	[1]8,100	9,520	2,500	7,200	10,000	11,000
CHLORIDE........	-	500	-	31	-	-	-
CARBONATE.......	-	[2]6,000	-	-	-	-	-
BICARBONATE.....	-	[2]11,000	-	-	-	-	-
TOTAL SULFUR....	-	[3]1,400	-	-	-	-	-

[1] 85 PERCENT FREE NH_3

[2] NOT FROM SAME ANALYSIS

[3] $S^{=}$ = 400
$SO_3^{=}$ = 300
$SO_4^{=}$ = 1,400
$S_2O_3^{=}$ = 1,000

The reference previously cited also forecasts 2.5 x 10^{15} Btu per year for synthetic gas produced from coal in the year 2000. If correct, there would be a need for about 31 plants each having a gas production capacity of 250 million cubic feet/day. This would have a major impact on the water and waste equipment manufacturing industry and on the entire economy because of the general stimulus it would have on industry. Each coal conversion plant in terms of 1976 dollars, was estimated by C. F. Braun to range in total cost from $0.87 to $1.28 billion.

A survey by Frost and Sullivan, Inc.[7] estimated that 20 plants would be in operation by 1990, producing 1.6 trillion cubic feet of gas/year. This is reasonably close to the 1.8 trillion cubic feet which would be the capacity of 20 plants each having capacity of 250 million cubic feet/day.

Attempting to relate projected expenditures for coal conversion plants to total sales for water and waste treatment equipment is difficult. Accurate information regarding the market for water and wastewater equipment has been virtually impossible to obtain since the Office of Business Research and Analysis of the Bureau of Domestic Commerce of the U.S. Department of Commerce discontinued maintaining summaries of water supply and wastewater disposal treatment equipment shipments. Annual reports of the major companies are consolidated and do not help very much. Published reports of expenditures or forecasts are either based upon total installed costs, including civil works, or do not indicate what is classified as equipment. In addition, the forecasts seldom indicate what dollars are used in the forecasts.

There have been predictions that equipment expenditures for water and waste treatment will be in the range between $1.5 and $2.0 billion in the 1980-1985 period. What may occur after that is highly speculative because water shortages in certain geographical areas probably will necessitate major expenditures for treatment of sewage plant effluents for industrial use. Enforcement of the zero effluent concept would also add appreciably to waste treatment equipment expenditures, so the long-range impact of coal conversion plants on the demand for water and waste treatment equipment cannot be predicted at this time.

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